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Three Ternary Rare Earth(III) Complexes Based on 3-[(4,6-Dimethyl-2pyrimidinyl)thio]-propanoic Acid and 1,10-Phenanthroline: Synthesis, Crystal Structure and Antioxidant Activity

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Keywords: 1,10-Phenanthroline; 3-[(4,6-Dimethyl-2-pyrimidinyl)thio]-propanoic acid; Rare earths; Crystal structure; Antioxidant

Abstract. Three ternary rare earth [Nd^{III} (1), Sm^{III} (2) and Y^{III} (3)] complexes based on 3-[(4,6-dimethyl-2-pyrimidinyl)thio]-propanoic acid (HL) and 1,10-phenanthroline (Phen) were synthesized and characterized by IR and UV/Vis spectroscopy, TGA, and single-crystal X-ray diffraction. The crystal structures showed that complexes 1–3 contain dinuclear rare earth units bridged by four propionate groups and are of general formula [*REL*₃(Phen)]₂·*n*H₂O (for 1 and 2: n = 2; for 3: n = 0). All rare earth ions are nine-coordinate with distorted monocapped square antiprismatic coordination polyhedra. Complex 1 crys-

Introduction

In the past few years, transition metal complexes with pyrimidine derivatives were paid considerable attention thanks to the excellent biological activity of pyrimidine and its derivatives.^[1] As expected, these metal complexes own higher activity than free ligands in versatile areas, like antiproliferative activity,^[2] antimicrobial activity^[3] and antitumor activity.^[4] Owing to the capacity of inhibits hydroxyl radical formation, Phen, a well-known chelating ligand, could reduce the severity of alloxan-induced diabetes in rats and relieved alloxan-induced toxicity in human fibroblastas in culture.^[5] And former study have illustrated that the copper complexes of 1,10-phenanthroline (Phen) derivatives owns a remarkable superoxide anion dismutase activity, and this activity partly depends on the steric and field effects of ligands involved.^[6]

Despite the excellent antitumor activity of pyrimidine, to the best of our knowledge, few scientists pay attention on the antioxidant activity of ternary rare earth complex with pyrimidine derivatives and 1,10-phenanthroline. Meanwhile, former researchers have proved that free radicals may impair human body through damaging the nucleic acid, protein etc.^[7] Hence, in this paper, three new ternary rare earth complexes based on tallizes in the monoclinic system, space group $P2_1/c$ with a = 16.241(7) Å, b = 16.095(7) Å, c = 19.169(6) Å, $\beta = 121.48(2)^\circ$. Complex **2** crystallizes in the monoclinic system, space group $P2_1/c$ with a = 16.187(5) Å, b = 16.045(4) Å, c = 19.001(4) Å, $\beta = 120.956(18)^\circ$. Complex **3** crystallizes in the triclinic system, space group P1 with a = 11.390(6) Å, b = 13.636(6) Å, c = 15.958(7) Å, $a = 72.310(17)^\circ$, $\beta = 77.548(15)^\circ$, $\gamma = 78.288(16)^\circ$. The antioxidant activity test shows that all complexes own higher antioxidant activity than free ligands.

3-[(4,6-dimethyl-2-pyrimidinyl)thio]-propanoic acid (HL) and Phen were synthesized and characterized by IR, UV/Vis, TGA, and single-crystal X-ray diffraction. The super oxide (O_2^-) dismutase activity was carried out by the pyrogallol autoxidation method.

Results and Discussion

All complexes are stable in air at room temperature and soluble in CH_2Cl_2 , dimethyl formamide (DMF), and dimethyl sulfoxide (DMSO), but insoluble in water, ethanol, ethyl acetate, cyclohexane, cyclohexanone, acrylonitrile, and ether.

IR Spectroscopy

The values of main IR absorption peaks in the spectra of the ligands and complexes are listed in Table 1. IR spectra of the three complexes were similar, but differed from those of the free ligands. For carboxylic acid, the characteristic peak of v(C=O) disappeared and was substituted by the symmetric stretching vibration (v_s) peak and asymmetric stretching vibration peak (v_{as}) after deprotonation, and this phenomenon could be proved in the spectrum of sodium salt of HL. In the complexes **1–3** spectra, the peak of v(C=O) (1706 cm⁻¹) in HL spectra disappeared and was replaced by asymmetric stretching peaks v_{as} (1540–1549 cm⁻¹) and symmetric stretching peaks v_s (1426–1427 cm⁻¹), which proved that L⁻ coordinates with *RE*^{III} through carboxyl group.^[4] The characteristic peaks of Phen can be found in the spectra of complexes and confirmed after compared with homoleptic complexes of *RE*^{III} and HL.

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Compound	v(Phen)				v(HL)						v(OH)
	v(C=C)	$\delta(C-C)$	δ(C–H)	$v(RE-N)^{a)}$	v(Me)	$\nu(Py)^{b)}$	Vas	Vs	v(C=O)	v(<i>RE</i> -O) ^{a)}	
Phen	1618	841	733	_	-	_	_	_	_	_	-
HL	_	_	-	_	2927	1585	_	_	1706	_	-
NaL ^{c)}	-	_	-	_	2927	1590	1537	1413	_	_	-
1	1600	846	731	544	2921	1582	1544	1426	_	418	3421
2	1603	846	731	544	2925	1581	1549	1427	_	418	3421
3	1608	846	730	544	2922	1581	1540	1427	_	418	_

Table 1. Main IR absorption peaks $/cm^{-1}$ of ligands and complexes 1–3.

a) RE = Rare earth. b) Py = Pyrimidine ring. c) NaL = sodium salt of 3-[(4,6-dimethyl-2-pyrimidinyl)thio]-propanoic acid.

There are shifts for v(C=C) from 1618 cm⁻¹ (free ligand) to about 1600–1608 cm⁻¹ (complexes), and δ (C–H) from 733 cm⁻¹ (free ligand) to 730–731 cm⁻¹ (complexes), which indicates that the Phen ligand coordinates with rare earth ions through nitrogen atoms.^[8] The new peaks of *RE*–N (544 cm⁻¹) and *RE*–O (418 cm⁻¹) in the spectra of the complexes further proved the coordination of Phen and HL with *RE*^{III}.^[9] The broad peak (3421 cm⁻¹) in the spectra of **1** and **2** belongs to lattice water.^[4] All the above results can be further confirmed by single-crystal X-ray diffraction.

UV/Vis Spectroscopy

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Figure 1 shows the UV/Vis spectra of the free ligands, the sodium salt of HL, and complexes 1–3 from 235 nm to 340 nm. The maximum absorption wavelengths (λ_{max}) of HL and Phen are at 248.8 nm and 264.6 nm, respectively. Meanwhile, the spectrum of deprotonated HL was measured with a tiny red shift (0.8 nm) to 249.6 nm. The λ_{max} values of complexes 1–3 are almost the same: 254.8 nm (1), 254.8 nm (2), and 254.6 nm (3), which assigned to an intramolecular charge transfer interaction and indicated that both L⁻ group and Phen are coordinated with rare earth ions successfully.^[10]



Figure 1. UV/Vis spectra of the ligands and complexes 1-3.

Thermogravimetric Analysis

Thermogravimetric analysis of complexes 1-3 are shown in Figure 2. The weight loss of complexes 1 and 2 (for 1: obsd. 2.1%, calcd. 1.9%; for 2: obsd. 2.1%, calcd. 1.8%) from 30

to 180 °C belongs to the remove of two lattice water molecules.^[11] No weight loss was found in this region for **3**, which indicated that no water molecules exist. These results are well consistent with the X-ray crystal structure. The decomposition of coordination framework starts at about 217 °C (**1**), 217 °C (**2**), and 218 °C (**3**).



Figure 2. Thermogravimetric curves of complexes 1-3.

Description of the Crystal Structures

The details of crystallographic data of 1-3 are listed in Table 2. Some selected interatomic distances are compiled in Table 3. The selected interatomic angles are listed in Table S1 (see Supporting Information).

The structures of complexes 1 and 2 are isostructural with space group $P2_1/c$ (Figure 3a for 1, Figure 4a for 2). Rare earth ions are nine-coordinate forming a very common distorted mono-capped square antiprism (Figure 3b for 1, Figure 4b for 2), which could be found in the reported lanthanide complexes $[Ln(PDA)_3(H_2O)]$ ·2H₂O [Ln = Nd, Sm] and $[Nd(\alpha -$ C₁₀H₇CH₂COO)₃(C₁₂H₈N₂)]₂ as well.^[12] Two rare earth ions are bridged by four L⁻ groups with bidentate bridging mode and tridentate bridging mode. The remaining L⁻ groups and Phen coordinated with the central metal ions as bidentate chelating group through oxygen atoms and nitrogen atoms, respectively. The distances of Nd(Sm)-O bonds are in the range of 2.418 Å to 2.589 Å (Sm–O bond: 2.391 Å to 2.557 Å) and the mean distance of the Nd(Sm)-N bond is 2.653 Å (Sm-N bond: 2.612 Å). Bidentate bridging groups own the largest O-C-O angles (1: O1-C13-O2, 125.4°; 2: O5-C31-O6, 125.4°), and



Table 2. Crystallographic data for complexes 1-3.

	1	2	3
Empirical formula	C ₇₈ H ₈₆ N ₁₆ Nd ₂ O ₁₄ S ₆	C ₇₈ H ₈₆ N ₁₆ O ₁₄ S ₆ Sm ₂	$C_{78}H_{82}N_{16}O_{12}S_6Y_2$
Formula weight	1952.47	1964.69	1805.78
Crystal system	monoclinic	monoclinic	triclinic
T/K	294(2)	294(2)	294(2)
Space group	$P2_1/c$	$P2_{1}/c$	P1
a /Å	16.241(7)	16.187(5)	11.390(6)
b /Å	16.095(7)	16.045(4)	13.636(6)
c /Å	19.169(6)	19.001(4)	15.958(7)
a /°	90	90	72.310(17)
β /°	121.48(2)	120.956(18)	77.548(15)
γ /°	90	90	78.288(16)
Volume /Å ³	4273(3)	4232.0(19)	2280.3(18)
$\rho / \text{g} \cdot \text{cm}^{-3}$	1.517	1.542	1.315
Crystal size /mm ³	$0.30 \times 0.13 \times 0.05$	$0.29 \times 0.13 \times 0.04$	$0.23 \times 0.17 \times 0.14$
Z	2	2	2
F(000)	1988	1996	932
μ /mm ⁻¹	1.419	1.593	1.467
Index ranges	$-19 \le h \le 19$	$-20 \le h \le 20$	$-13 \le h \le 13$
	$-19 \le k \le 19$	$-20 \le k \le 20$	$-16 \le k \le 15$
	$-22 \le l \le 22$	$-24 \le l \le 24$	$-18 \le l \le 18$
Data/restraints/ parameters	7537 / 2 / 529	9666 / 0 / 538	8033 / 0 / 520
Max. and min. transmission	0.9324, 0.6756	0.9390, 0.6551	0.8210, 0.7291
Reflections collected / unique	36144 / 7537 [<i>R</i> (int) = 0.0977]	43676 / 9666 [R(int) = 0.0716]	19725 / 8033 [R(int) = 0.0586]
GOF	1.050	1.060	1.096
$R_1, wR_2 [I > 2\sigma(I)]$	0.0446, 0.1100	0.0396, 0.0969	0.0539, 0.1749
R_1 , wR_2 (all data)	0.0503, 0.1172	0.0478, 0.1042	0.0598, 0.1811
Largest diff peak and hole / e·Å ⁻³	1.896 and -1.374	1.732 and -1.109	1.524 and -0.448

Table 3. Selected interatomic distances /Å for complexes 1-3.

1							
Nd(1)-O(2) ^{#1} Nd(1)-O(5) ^{#1} Nd(1)-O(1) Symmetry code	2.418(3) 2.419(3) 2.444(3) s: #1 -x,-y+2,-z+1	Nd(1)-O(6) Nd(1)-O(5) Nd(1)-Nd(1) ^{#1}	2.567(3) 2.589(3) 3.9998(13)	Nd(1)–O(4) Nd(1)–O(3)	2.478(3) 2.540(3)	Nd(1)–N(1) Nd(1)–N(2)	2.630(4) 2.676(4)
2							
Sm(1)–O(5) Sm(1)–O(1) ^{#1} Sm(1)–O(6) ^{#1} Symmetry code	2.391(2) 2.392(2) 2.403(2) s: #1 -x, -y+2, -z-	Sm(1)–O(2) Sm(1)–O(1) Sm(1)–Sm(1) ^{#1} +1.	2.555(3) 2.557(2) 3.9622(8)	Sm(1)–O(4) Sm(1)–O(3)	2.446(3) 2.521(3)	Sm(1)–N(1) Sm(1)–N(2)	2.597(3) 2.640(3)
3							
Y(1)-O(4) ^{#1} Y(1)-O(5) ^{#1} Y(1)-O(3) Symmetry code	2.307(3) 2.316(3) 2.352(3) s: #1 -x, -y+1, -z-	Y(1)-O(1) Y(1)-O(5) Y(1)-Y(1) ^{#1} +1.	2.530(3) 2.570(3) 3.9261(15)	Y(1)–O(2) Y(1)–O(6)	2.375(3) 2.412(3)	Y(1)–N(1) Y(1)–N(2)	2.605(3) 2.559(3)

the next are bidentate chelating groups (1: O3–C22–O4, 121.7°; **2**: O3–C22–O4, 121.3°) and tridentate bridging groups (1: O5–C31–O6, 120.3°; **2**: O1–C13–O2, 120.6°). The coordination number, coordination arrangement, and the interatomic distances and angles in complexes **1** and **2** are similar to the statistics found in the published ternary rare earth complexes $[Nd(2-Cl-4,5-dfba)_3PhenH_2O]_2$ and $[Sm(o-MBA)_3Phen]_2$.^[13]

With respect to complex **3**, Figure 5a and b show the molecular structure of complex **3** and the coordination arrangement of the Y^{III} ion, respectively. Complex **3** is a dual core structure with space group *P*1 and two Y^{III} ions are bridged together by four L⁻ groups, with two of them in bidentate bridging mode and the remaining two in tridentate bridging mode. The bidentate chelating mode could be found between Y^{III} ions and the left L^- group or Phen molecule. It is obvious that the coordination environment of Y^{III} is similar to Nd^{III} and Sm^{III}.

The Y–O interatomic distances range from 2.307 Å to 2.570 Å and the mean distance of Y–N bond is 2.582 Å. Compared with tridentate bridging group (O5–C31–O6: 120.0°) and bidentate chelating group (O1–C13–O2: 120.6°), the bidentate bridging group (O3–C22–O4: 126.3°) owns the largest O–C–O angle. The structure of complex **3** is similar to that of reported ternary rare earth complexes $Y_2(\text{crot})_6(\text{Phen})_2\cdot 2H_2O$ and $Y_2(\text{crot})_6(\text{mPhen})_2\cdot 2H_2O$.^[14] π – π interactions just exist in **3** between Phen of nearby molecules with a centroid-centroid distance of 3.667(4) Å (Figure 6).



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Figure 3. (a) Crystal structure of $[NdL_3(Phen)]_2 \cdot 2H_2O$ (1). Hydrogen atoms and lattice water molecules are omitted for clarity; (b) coordination arrangement of the Nd^{III} atom in 1.



Figure 4. (a) Crystal structure of $[SmL_3(Phen)]_2 \cdot 2H_2O$ (2). Hydrogen atoms and lattice water molecules are omitted for clarity; (b) coordination arrangement of the Sm^{III} atom in 2.



Figure 5. (a) Crystal structure of $[YL_3(Phen)]_2$ (3). Hydrogen atoms are omitted for clarity; b) coordination arrangement of the Y^{III} atom in 3.



Figure 6. π - π interactions in complex **3**. Hydrogen atoms and part of the L⁻ groups are omitted for clarity.

It is obvious that complex **3** has a different molecular structure compared with complex **1** and **2**. This difference may related to the π - π interactions existing in complex **3**, but the exact reasons of this difference still need to be further investigated. However, the coordination numbers of all the complexes are 9 and the coordination arrangements of the three complexes are completely the same: distorted mono-capped square antiprism with two nitrogen atoms from Phen molecule and seven oxygen atoms from L⁻ groups.

Antioxidant Activity

Some investigations have shown that compared with free ligand, their transition metal complexes may own a higher antioxidant activity.^[15] Hence, the antioxidant activities of free ligands and complexes **1–3** were investigated. Free ligand HL (IC₅₀ = 2.53 mmol·L⁻¹) expressed an obvious antioxidant activity. However, no noticeable activity was found for Phen under pyrogallol autoxidation method. As expected, the antioxidant activity tests illustrate that complexes **1–3** (for **1**: IC₅₀ = 0.11 mmol·L⁻¹; for **2**: IC₅₀ = 0.11 mmol·L⁻¹; for **3**: IC₅₀ = 0.10 mmol·L⁻¹) possess much higher activity than free ligand HL. Meanwhile, the antioxidant activity of complexes **1–3** is higher than the reported copper(II)-dipeptide complexes Cu(Gly·Ala)·2H₂O (8.00 mmol·L⁻¹) and Cu(Gly·Gly)·3H₂O (1.32 mmol·L⁻¹), but lower than Cu(glygly)(HPB)(Cl)·2H₂O (3.83 µmmol·L⁻¹).^[16]

It is believed that this conclusion may be helpful in preparing more high-performance antioxidants.

Conclusions

this work, a new ligand 3-[(4,6-dimethyl-2-In pyrimidinyl)thio]-propanoic acid was synthesized and its ternary rare earth [Nd^{III} (1), Sm^{III} (2) and Y(III) (3)] complexes based on 1,10-phenanthroline (Phen) were obtained and well characterized with IR, UV/Vis, TGA, and single X-ray diffraction. The three complexes have dinuclear structures in which two rare earth ions bridged by four L⁻ groups with a general formula of $[REL_3(Phen)]_2 \cdot nH_2O$ (for 1 and 2: n = 2; for 3: n= 0). Herein, pioneering work on the antioxidant activity of ternary rare earth complexes based on pyrimidine derivatives and 1,10-phenanthroline was done. Investigations on the super oxide (O_2^{-}) dismutase activity of free ligands and complexes 1-3 illustrated that the three complexes own higher activity than the free ligands HL and Phen, which confirms the former result that transition metal complexes may exhibit higher antioxidant activity than the corresponding free ligand. This conclusion provides a new way to prepare more effective antioxidants.

Experimental Section

Materials and General Methods: All starting reagents were commercially available as reagent grade and were used without further purification. Rare earth chlorides were prepared by the reaction of rare earth oxide (Yuelong, China) with HCl. Infrared (IR) spectra were recorded with an ALPHA FT-IR spectrometer (Bruker, Germany) in the region of 4000–400 cm⁻¹ by using KBr pellets. UV/Vis spectra were carried out with a UT-1901 (Persee, China) from 340 nm to 235 nm in CH₂Cl₂. Thermogravimetric analyses (TGA) were taken with a STA 409 PC (NETZSCH, Germany) in a nitrogen atmosphere from room temperature to 1000 °C with a heating rate of 10 K·min⁻¹. The single-crystal X-ray diffraction was carried out with a XtaLAB mini (Rigaku, Japan) at 294(2) K. The antioxidant activity of both free ligands and complexes was carried out by pyrogallol autoxidation method.

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Synthesis of 4,6-Dimethyl-2-pyrimidineethiol:^[4] An ethanol solution (60.0 mL) of thiourea (7.61 g, 100 mmol) and acetyl acetone (10.2 mL) was heated to reflux at 80 °C for 0.5 h. Afterwards concentrated HCl (16.8 mL) was added slowly. The reflux conditions were kept for further 2 h and the mixture was cooled to room temperature overnight. The yellow crystals were obtained with filtration, washed with a small amount of water and dried in vacuo. Yield: 62.1%.

Synthesis of 3-[(4,6-Dimethyl-2-pyrimidinyl)thio]-propanoic Acid: (see Figure 7) A distilled water (50.0 mL) solution of 3-chloropropionic acid (4.34 g, 40.0 mmol), NaOH (3.20 g, 80.0 mmol), and 4,6dimethyl-2-pyrimidineethiol (5.61 g, 40.0 mmol) was heated to reflux 80 °C for 1.5 h, filtered while hot, and cooled to room temperature. Afterwards, concentrated HCl was dropped to obtain the white precipitation. The white crystals were collected after recrystallized from 50% ethanol, filtered, washed with a small amount of water and dried in vacuo. Yield: 75.8%. **IR** (KBr): $\tilde{v} = 3697$ (s), 1706 (s), 1586 (s), 1535 (m), 1430 (m), 1340 (s), 1249 (s), 1164 (m), 950 (w), 887 (w), 859 (w), 815 (w), 547 (w) cm⁻¹. **UV/Vis** (λ_{max} , CH₂Cl₂): 248.8 nm.



Figure 7. Synthesis of ligand 3-[(4,6-dimethyl-2-pyrimidinyl)thio]-propanoic acid (HL).

Synthesis of $RE(Phen)_2Cl_3$:^[17] An ethanol solution (25.0 mL) of Phen•H₂O (0.79 g, 4.0 mmol) and $RECl_3$ ·6H₂O (2.0 mmol) was stirred for 2.0 h at room temperature. The white powder was obtained by filtration, washed with a small amount of ethanol and further dried in vacuo. Yield: 86.7% (1), 88.4% (2), 85.9% (3).

Synthesis of Complexes 1–3: HL (0.64 g, 3.0 mmol) was dissolved in 50% methanol (10.0 mL). Afterwards, $NH_3 \cdot H_2O$ was added until the pH arrived to 6.0. This mixture was added into the 50% methanol (15.0 mL) solution of *RE*(Phen)₂Cl₃ (1.0 mmol). The pH was kept at 6.0 using $NH_3 \cdot H_2O$, stirred at room temperature for 2.0 h, and filtered. After three weeks, the colorless block crystals of 1–3 suitable for Xray diffraction were obtained from filtrate by slow evaporation at room temp. Yield: 69.1% (1), 68.7% (2), 65.9% (3).

Antioxidant Activity: Pyrogallol autoxidized at a very high speed in aqueous alkaline medium, and several intermediate products and superoxide free radical were apparently formed.^[18] Owning to the existence of intermediate product, the aqueous solution became yellow

with a spectrum showing a very intensive peak at about 320 nm. The superoxide free radical inhibition activity of sample could be acquired after compared with the pyrogallol autoxidation rate.^[19]

The samples (1: 0.0269 g; 2: 0.0264 g; 3: 0.0266 g) were dissolved in DMF (1.0 mL) and diluted with water to 50.00 mL.

A mixture (5.00 mL), containing Tris-HCl (2.00 mL, pH = 8.3), distilled water (2.70 mL), and pyrogallol (0.30 mL, 6.0 mmol·L⁻¹) was transferred to the quartz absorption cells. The values of absorption, measured at 319.2 nm, were recorded for 4.0 min. The slope of absorption-time curve stands for the pyrogallol autoxidant rate (v_0).

Tris-HCl (2.00 mL, pH = 8.3) and the sample (0.10 mL, 0.20 mL, 0.50 mL, 1.0 mL, 1.5 mL, 2.0 mL, 2.5 mL) were mixed. Distilled water was added till the volume arrived at 4.70 mL. Pyrogallol (0.30 mL, 6.0 mmol·L⁻¹) was added into the mixture at last. The values of absorption, measured at 319.2 nm, were recorded for 4.0 min. The slopes of absorption-time curves stand for the sample antioxidant rate (v_{t}).

The inhibition ratio (Z) of samples could be calculated by the equation: $Z = (1 - v_t / v_0) \times 100 \%.^{[20]}$

The half maximal inhibitory concentration, short for IC_{50} , represents the concentration of an inhibitor that is required for 50% inhibition and is commonly used as a measure of sample effectiveness. For the antioxidant effectiveness of complexes **1–3**, the half maximal inhibitory concentration (IC_{50}) values could be calculated using the linear relation between the inhibitory ratio and concentration logarithm.^[21]

X-ray Single Crystal Structure Determination: The X-ray singlecrystal diffraction data of 1–3 were collected with a Rigaku XtaLAB mini diffractometer (Japan) at 294(2) K with graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å) and ω scan mode. The semi-empirical multi scan absorption correction was applied to the X-ray data of 1–3. All the structures were solved by direct method and refined by full-matrix least-squares methods with SHELXL package.^[22] Hydrogen atoms of complexes 1–3 were positioned at geometrically calculated positions and refined with fixed isotropic thermal parameters.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1035513 (1), CCDC-1035514 (2), and CCDC-1035515 (3) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): Selected interatomic angles of complexes **1–3**.

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