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Lanthanide (III) Morpholine 4-Dithiocarbamate Complexes: Pr(III) Derivative Shows First Example of Polymeric Lanthanide(III) Dithiocarbamate

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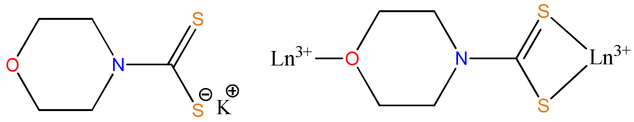
Three lanthanide(III) morpholine 4-dithiocarbamate complexes [Ln(Phen)(Mph-Dtc)$_3$]· x CH_2Cl_2 [Ln = Pr (**1**), Nd (**2**) and Eu (**3**); Mph-Dtc = morpholine 4-dithiocarbamate; x = 2 (**1**) or 1 (**2**-**3**)] have been prepared from the reaction of potassium salt of morpholine 4-dithiocarbamate with lanthanide nitrates and phenanthroline. Complexes **1**-**3** were characterized by varoius analytical techniques and their solid state structures were established by single crystal X-ray diffraction analysis. The Ln(III) ions are nine or eight coordinated in **1** and **2**-**3** respectively. Interestingly, oxygen atom of one of the three coordinated Mph-Dtc ligands is further coordinated to a Pr(III) ion of the adjacent molecule. Thus, it results in the formation of an one-dimensional (1D) polymeric structure. Thermal stability and optical properties of **1**-**3** have been investigated.

Introduction

Recently, a tremendous attention has been paid to the synthesis of lanthanide based complexes and frameworks.[1, 2] These compounds find important applications in different areas such as optical probes,[3] magnetism,[4-6] catalysis,[7] gas adsorption[8] and biology.[9] A varieties of ligands have been employed to synthesize lanthanide complexes. In this context, dithiocarbamates (Dtc) are an important class of ligands with soft sulfur donor atoms. Mostly, dithiocarbamates reacts with lanthanide(III) ion to form neutral [Ln(Dtc)$_3$L] complexes [L = 2,2'-bipyidine or 1,10-phenanthroline]. However, neutral [Ln(Dtc)$_3$] or anionic [Ln(Dtc)$_4$]$^-$ can be found in the literature.[10] These lanthanide complexes of Dtc are important precursors for the synthesis of lanthanide sulfide and magnetic nanomaterials.[11] For instance, lanthanide sulfides were prepared from the decomposition of [Ln(S$_2$CNEt$_2$)$_3$·phen] (Ln = La-Lu; Et = ethyl; phen = phenanthroline).[12, 13] The Eu(III) and Gd(III) dithiocarbamate complexes are effective precursors for the synthesis of mixed (doped) Eu$_{1-x}$Gd$_x$ nanocrystals with a variable ratio of Gd to Eu.[14, 15] Very recently, a series of lanthanide(III) piperidine dithiocarbamate complexes have been synthesized and photoluminescence properties of piperidine dithiocarbamate complexes of Sm(III), Pr(III), Tb(III), Dy(III) have been investigated.[16] Room temperature photoluminescence properties of Sm(III) and Pr(III) dithiocarbamates were also reported.[17] Moreover, lanthanide(III) dithiocarbamate complexes were proven to be an effective catalyst for the asymmetric cyanation of aromatic aldehydes.[16, 18] Lanthanide(III) azepane dithiocarbamate complexes were synthesized and their optical, catalytic properties were reported.[19] In spite of these reports, lanthanide (III) dithiocarbamate complexes are fewer when compared with lanthanide (III) complexes of other organic ligands containing oxygen and nitrogen donor atoms. Therefore, a lot of research works are left in this area. To the best of our knowledge, there is no report of polymeric lanthanide(III) dithiocarbamate complex in the literature.

Against these background, we are involved in the synthesis of discrete and polymeric lanthanide(III) dithiocarbamate complexes. We have chosen potassium salt of morpholine 4-dithiocarbamate for our work (Scheme 1). It can coordinate to lanthanide(III) ion by two sulfur atoms as well as with one oxygen atom.



Scheme 1: Potassium salt of morpholine 4-dithiocarbamate (Mph-Dtc) and its coordination modes.

In this paper, we report syntheses, characterizations and structures of three lanthanide(III) morpholine 4-dithiocarbamate complexes [Ln(Phen)(Mph-Dtc)$_3$]· x CH_2Cl_2 [Ln = Pr (**1**), Nd (**2**) and Eu (**3**); Mph-Dtc = morpholine 4-dithiocarbamate; x = 2 (**1**) or 1 (**2**-**3**)]. The thermal stability and optical properties of **1**-**3** have also been discussed.

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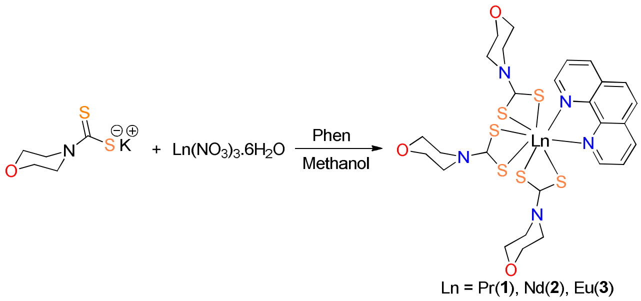
Results and discussion

Potassium salt of morpholine 4-dithiocarbamate has been prepared by the reaction of morpholine with carbon disulphide in presence of potassium hydroxide following the reported method.[20] Complexes [Ln(Phen)(Mph-Dtc)$_3$]· x CH_2Cl_2 [Ln = Pr (**1**), Nd (**2**) and Eu (**3**); Mph-Dtc = morpholine 4-dithiocarbamate; x = 2 (**1**) or 1 (**2**-**3**)] were prepared by treating potassium salt of Mph-Dtc with hydrated lanthanide(III) nitrate in the presence of phenanthroline in methanol at room temperature (Scheme 2). Pure single crystals of **1**-**3** are obtained by diffusing petroleum ether into a dichloromethane solution of **1**-**3**. Details of experimental procedures are given in the experimental section.



Scheme 2: Synthesis of complexes **1**-**3**.

All complexes were characterized by conventional analytical and spectroscopic techniques. The solid state structures of **1**-**3** were determined by single crystal X-ray diffraction analyses. Complex **1**, [Pr(Phen)(Mph-Dtc)$_3$]·2CH_2Cl_2 crystallizes in the monoclinic space group P2$_1$/c with four formula units per unit cell. Complex **2**-**3** crystallize in the triclinic space group P-1 with two molecules per unit cell. Figure 1 shows the molecular structure of **1**-**3**. Dichloromethane molecules are not shown for clarity. Details of single crystal X-ray diffraction analyses are given in table 1. The Pr(III) ion is nine coordinated in **1** (Figure 1a). Six sulfur atoms (S1-S6) of three Mph-Dtc ligands are bonded to Pr(III) ion with Pr-S bond lengths of 2.9192(16)-2.9960(15) Å which are longer than the reported values.[16, 17] Thus each Mph-Dtc ligand behaves as bidentate ligand with a S-Pr-S bite angle of 59.24(4)-60.00(4)°. Phenanthroline ligand is coordinated to Pr(III) ion with the two nitrogen atoms (N1 and N2) with bond lengths of 2.674(4)-2.690(4) Å which are in close agreement with the literature values.[19] Most interesting feature of the structure of **1** is that one oxygen atom (O2) of one of the three Mph-Dtc ligand of [Pr(Phen)(Mph-Dtc)$_3$] molecule is further coordinated to

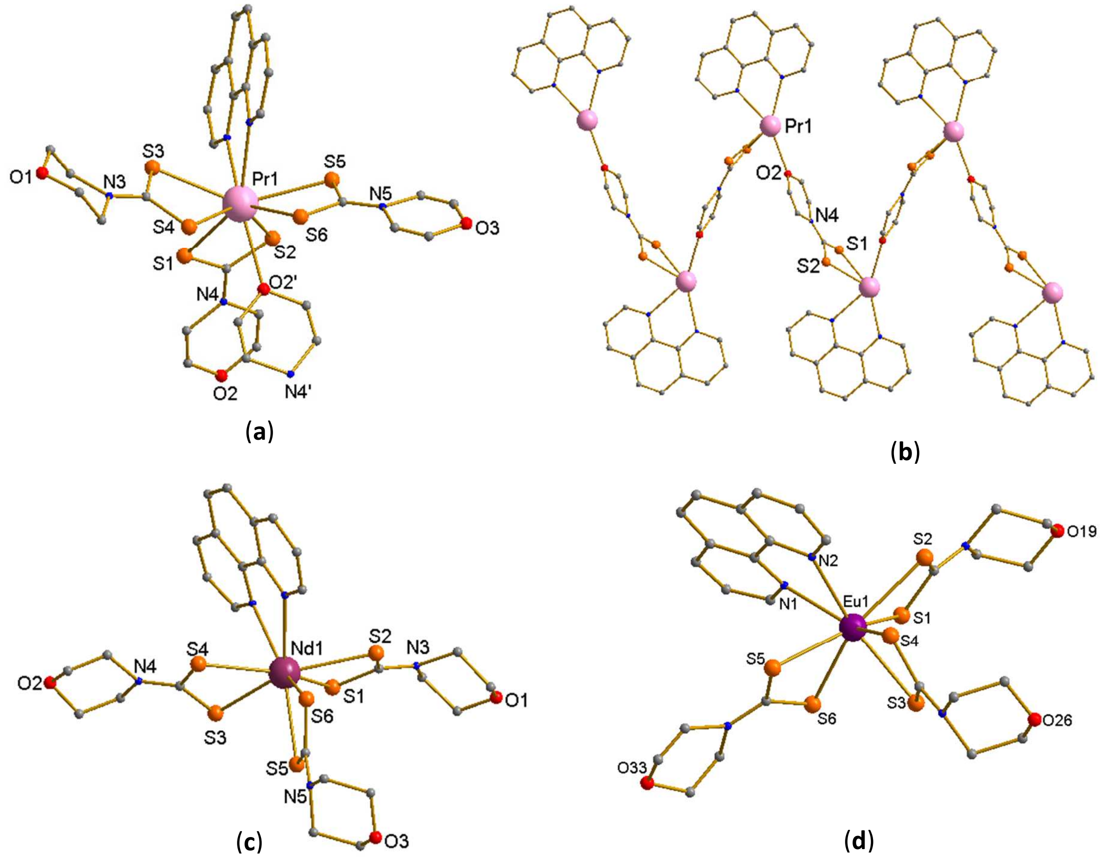


Figure 1: (a) Molecular structure of **1**. (b) One dimensional zigzag polymer of **1**. Other Mph-Dtc ligands bonded to Pr(III) ion are not shown for clarity. (c) Molecular structure of **2** (d) molecular structure of **3**. Dichloromethane molecules and hydrogen atoms are not shown for clarity.

Table 1 Single crystal data and structure refinement parameters for complexes **1**-**3**.

Compound	1	2	3
Formula	$C_{29}H_{36}Cl_4N_5O_3PrS_6$	$C_{28}H_{34}Cl_2N_5O_3NdS_6$	$C_{28}H_{34}Cl_2N_5O_3EuS_6$
Formula mass	977.70	896.10	903.82
T/K	293(2)	293(2)	100(2)
λ/Å	0.71073	0.71073	0.71073
Crystal dimensions/mm	0.20×0.17×0.12	0.19×0.15×0.10	0.28×0.14×0.09
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	P-1	P-1
a/Å	17.8590(4)	10.783(7)	10.6899(5)
b/Å	10.2274(3)	10.922(8)	10.7180(5)
c/Å	27.1517(7)	17.282(13)	16.9914(8)
α/°	90.00	78.322(7)	78.016(2)
β/°	128.03(2)	88.233(6)	88.254(2)
γ/°	90.00	65.392(7)	65.530(2)
V/Å^3	3906.00(19)	1808.9(2)	1729.92(14)
Z	4	2	2
D_c/g cm^{-3}	1.663	1.645	1.735
μ/mm^{-1}	1.880	1.967	2.369
F(000)	1968	902	908
θ Range/$^\circ$	2.46- 27.00	3.00-27.00	2.225-25.308
Measured reflections	33541	27064	28817
Independent reflections/Rint	8482/0.0547	7829/0.0529	6276/0.0265
Parameters	519	406	461
R_1 ($I > 2\sigma(I)$)^a	0.0541	0.0380	0.0188
wR_2 (all data)^b	0.1305	0.0835	0.0489
Goodness-of-fit on F^2	1.058	1.006	1.048
$\Delta\rho_{max, min}$/e Å^{-3}	1.103, -0.827	0.857, -0.766	0.665, -0.373

Table 2 Selected bond lengths (Å) and angles (°) of complexes **1**-**3**.

Bond/Angle	**1 (Ln = Pr)**	**2 (Ln = Nd)**	**3 (Ln = Eu)**
Ln-S1	2.9192(16)	2.9343(11)	2.8930(6)
Ln-S2	2.9960(15)	2.8904(10)	2.8340(6)
Ln-S3	2.9785(15)	2.8895(10)	2.8348(6)
Ln-S4	2.9578(16)	2.8516(10)	2.8766(6)
Ln-S5	2.9554(15)	2.8796(11)	2.7977(6)
Ln-S6	2.9704(15)	2.9145(11)	2.8533(6)
Ln-N1	2.690(4)	2.665(3)	2.605(2)
Ln-N2	2.674(4)	2.660(3)	2.613(2)
Ln-O	2.739(4)	-	-
S1-Ln-S2	59.79(4)	61.11(3)	62.251(16)
S3-Ln-S4	59.24(4)	62.29(3)	62.212(17)
S5-Ln-S6	60.00(4)	61.27(3)	63.334(17)
N1-Ln-N2	61.65(13)	61.68(10)	62.96(6)

adjacent with symmetry related (9-x, y+1/2, -z+3/2) Pr(III) ion. The Pr-O bond length is 2.739(4) Å. Thus, it forms a one dimensional (1D) zigzag polymer of **1** (figure 1b and S1). To the best of our knowledge, complex **1** is the first representative of lanthanide(III) dithiocarbamate polymer. Detailed bond lengths and bond angles of **1** are provided in table 2. Complex **2**, [Nd(Phen)(Mph-Dtc)$_3$]·CH_2Cl_2 and **3**, [Eu(Phen)(Mph-Dtc)$_3$]·CH_2Cl_2 are isostructural. Therefore, solid state structure of **2** is discussed as a representative of **2** and **3**. Interestingly, Nd(III) ion is eight coordinated by six sulfur atoms (S1-S6) of three Mph-Dtc ligands and two nitrogen atoms (N1 and N2) of a phenanthroline ligand. The Nd-S and Nd-N bond lengths are in the range of 2.8516(9)- 2.9343(11) Å and 2.661(3)- 2.665(3) Å respectively. The S-Nd-S bite angles lie in the range of 61.11(3)-62.29(3)$^\circ$. These values are very close to the observed values.[12, 16] Figures S2-S4 four show the molecular packing of **1**-**3** within the unit cell respectively.

The thermal stability of complexes **1**-**3** have been investigated by thermogravimetric analysis (TGA). Figure 2 shows the TG curve of **1**-**3**. The TG curves show an initial weight loss up to 130 $^\circ$C because of removal of free dichloromethane molecules from **1**-**3**. The complexes start to decompose on further heating. In case of complexes **1**-**2**, the final weight corresponds to a mass of one Ln and 1.5 of sulfur.

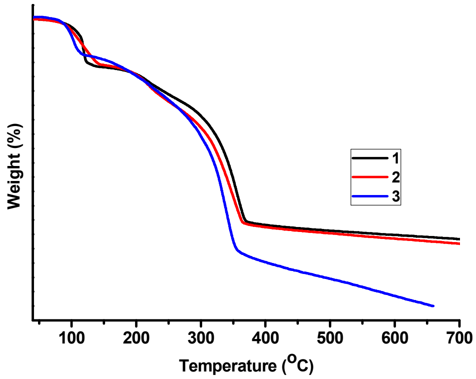


Figure 2: TG curves of **1**-**3**.

However, complex **3** continues to decompose slowly above this decomposition temperature. This suggests the conversion of lanthanide sulfides to oxides or oxysulfides.[13]

Electronic absorption spectra of complexes **1**-**3** are recorded in acetonitrile. The spectra of **1**-**3** exhibit a similar pattern in the UV region. Figure 3-5 show the absorption spectrum of complexes of **1**-**3**. A band approximately at 230 nm and at 263 nm appear in the absorption spectra of all complexes. The first band is assigned to a π to π* electronic transition of the bidentate phenanthroline ligand. Second band at 263 nm is because of combined effect of the n to π* electronic transition of the phenanthroline ligand and the N-CS_2 chromophore of the Mph-Dtc ligands (figure S5).[17] The visible region of the absorption spectra of **1**-**2** show a number of weak and narrow bands resulted from the Laporte-forbidden f to f transitions of the lanthanide (III) ions. These bands are assigned with respect to the absorption spectra of the lanthanide(III) aquo ions.[21-23] The bands observed due to the f-f electronic transition of complex **1** are attributed to transitions from the ground state $^3H_4$ of Pr(III) ion to $^3P_2$ (456 nm), $^3P_1$ (481 nm), $^3P_0$ (498 nm) and $^1D_2$ (604 nm) states (Figure 3).[10]

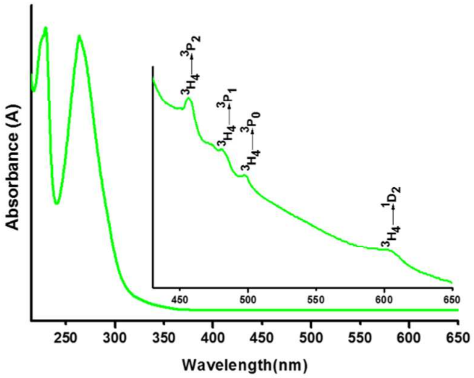


Figure 3: UV-vis absorption spectrum of **1.** Weak f-f transitions are shown in the inset.

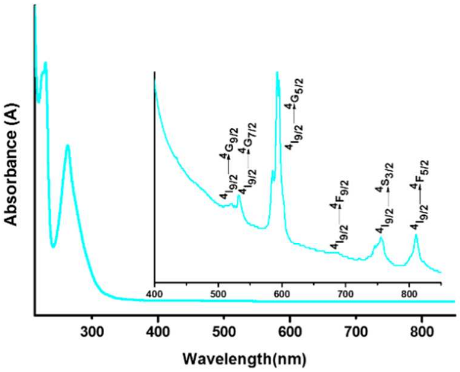


Figure 4: UV-vis absorption spectrum of **2**. Weak f-f transitions are shown in the inset.

For complex **2**, the bands in the visible region correspond to transitions from the ground state $^4I_{9/2}$ to $^4G_{9/2}$ (519 nm), $^4G_{7/2}$ (531 nm), $^4G_{5/2}$ (592 nm), $^4F_{9/2}$ (687 nm), $^4S_{3/2}$ (755 nm) and $^4F_{5/2}$ (810 nm) (Figure 4). Interestingly, no f-f transition bands are observed for complex **3** at room temperature. Instead, a ligand to metal charge transfer (LMCT) band at 450 nm is observed (Figure 5) because of reduction of Eu^{3+} by strongly reducing dithiocarbamate ligands. This is further supported by the deep garnet colour of **3**.[24] Thus, it differs from complexes **1**-**2** which show characteristic pale colours of their corresponding lanthanide (III) ions.[12] The solid state diffuse reflectance spectra of complexes **1**-**3** were measured (figure S6-S8). The solid state spectra support the observations that found when the spectra of **1**-**3** were recorded in solution.

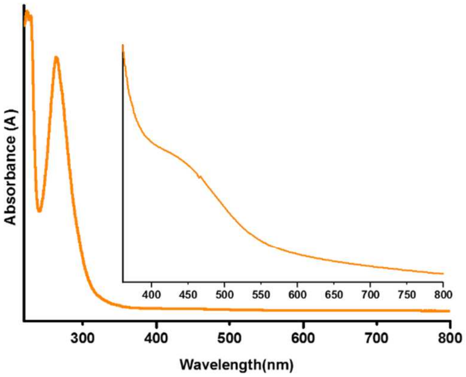


Figure 5: UV-vis absorption spectrum of **3**.

Conclusions

Three lanthanide(III) morpholine 4-dithiocarbamate complexes [Ln(Phen)(Mph-Dtc)$_3$]· x CH_2Cl_2 [Ln = Pr (**1**), Nd (**2**) and Eu (**3**) were synthesized and characterized. The solid state structure determination demonstrate the formation of polymeric (**1**) or discrete (**2**-**3**) lanthanide(III) dithiocarbamate complexes. Complex **1** is the first example of polymeric lanthanide(III) dithiocarbamate. Electronic absorption spectra of all complexes show predominately ligand centred transitions. Laporte forbidden f-f transitions were observed for **1**-**2**. However, LMCT transition was observed in the UV-vis spectrum of complex **3**. Present investigation includes the syntheses of lanthanide(III) organic frameworks based on dithiocarbamate ligands and will be reported in future.

Experimental

All synthetic work was performed under aerobic condition. Solvents were distilled prior to use. Commercially available reagents were used as received. The ligand, potassium salt of morpholine 4-dithiocarbamate has been prepared by following earlier method with a slight modification.[19] Potassium hydroxide (25 mmol, 1.401 g) was dissolved in 3 mL of distilled water in an ice bath and 50 mL of ethanol was added to it. Morpholine (25 mmol, 2.178 mL) was then added dropwise to it. Finally, carbon disulphide (25 mmol,1.507 mL) was added dropwise to the reaction medium which yielded an immediate heavy precipitation. It was stirred for 15 minutes further. The precipitate was collected through filtration and washed with cold methanol. The resulting solid was used for the synthesis of lanthanide(III) dithiocarbamate complexes without further purifications.

General procedure for syntheses of complexes 1-3

All of the three [Ln(Mph-Dtc)$_3$(Phen)] complexes where Ln = Pr, Nd, Eu (**1, 2** and **3**) were synthesizd by following identical experimental procedure. A methanolic solution of phenanthroline (0.165 mmol, 0.032 g) was added dropwise to a methanolic solution of respective Ln(NO$_3$)$_3$·6H$_2$O (0.165 mmol). The mixture was stirred for 10 minutes. A methanolic solution of potassium morpholine 4-dithiocarbamate (0.5 mmol, 0.1 g) was added dropwise to it and stirred for 15 minutes. The resulting solid was filtered, washed with methanol and kept for air drying. Single crystals suitable for single crystal X-ray diffraction were obtained by diffusing petrolium ether into dichloromethane solution of lanthanide(III) dithiocarbamate. The complexes were fairly soluble in chloroform, dichloromethane, DMF and DMSO.

[Pr(Phen)(Mph-Dtc)$_3$]·2CH$_2$Cl$_2$ (1): Pale green solid. Yield: 0.097 g (65.0 %). IR (KBr, cm^{-1}): 3406 (br), 3032 (w), 2964 (w), 2893 (w), 2854 (w), 2476 (w), 1980 (w), 1623 (w), 1588 (w), 1570 (w), 1512 (m), 1459 (s), 1419 (s), 1350 (w), 1300 (w), 1263 (s), 1214 (s), 1140 (w), 1110 (s), 1065 (w), 1021 (s), 1006 (s), 901 (w), 871 (w), 844 (m), 824 (m), 728 (m), 636 (w), 546 (s), 419 (m). Anal. Calc. for $C_{29}H_{36}Cl_4N_5O_3PrS_6$: C 35.62; H 3.71; N 7.16. Found: C 35.67; H 3.46; N 7.24.

[Nd(Phen)(Mph-Dtc)$_3$]·CH$_2$Cl$_2$ (2): Pale blue solid. Yield: 0.113 g (82.4 %). IR (KBr, cm^{-1}): 3409 (br), 3046 (w), 2963 (w), 2893 (m), 2852 (m), 2719 (w), 2478 (w), 1980 (w), 1624 (w), 1588 (w), 1571 (w), 1514 (m), 1459 (s), 1420 (s), 1384 (m), 1353 (w), 1299 (w), 1264 (s), 1215 (s), 1140 (w), 1064 (w), 1022 (s), 1001 (s), 901 (w), 872 (w), 862 (w), 845 (m), 826 (w), 845 (m), 826 (w), 773 (w), 728 (m), 636 (w), 587 (w), 546 (s), 443 (w), 419 (w). Anal. Calc. for $C_{28}H_{34}Cl_2N_5NdO_3S_6$: C 37.53, H 3.82, N 7.82. Found: C 37.16; H 3.71; N 7.68.

[Eu(Phen)(Mph-Dtc)$_3$]·CH$_2$Cl$_2$ (3): Orange red solid. Yield: 0.104 g (75.0%). IR (KBr, cm^{-1}): 3432 (br), 3032 (w), 2961 (w), 2904 (w), 2846 (w), 2751 (w), 2479 (w), 1977 (w), 1624 (w), 1588 (w), 1572 (w), 1515 (m), 1465 (s), 1422 (s), 1383 (w), 1354 (w), 1264 (s), 1222 (s), 1139 (w), 1110 (s), 1023 (s), 1000 (s), 899 (w), 872 (w), 862 (w), 838 (w), 827 (w), 763 (w), 729 (s), 699 (w), 636 (w), 545 (m), 443 (w), 419 (w). Anal. Calc. for $C_{28}H_{34}Cl_2N_5EuO_3S_6$: C 37.21, H 3.79, N 7.75. Found: C 37.30; H 3.48; N 7.63.

Analytical techniques

Elemental analyses were performed on a VARIO MICRO cube analyser by Elemental analyser system GMBH. IR spectra in KBr (4500-500 cm^{-1}) were recorded using a Perkin–Elmer RXI FT-IR spectrometer. The electronic spectra of **1**-**3** and ligands were recorded with a Shimadzu UV-1800 spectrometer. Solid-state reflectance spectra of **1**-**3** were recorded in a Cary-5000 UV-VIS-NIR spectrometer. Thermogravimetric analyses (TGA) were performed with a NETZSCH leading Thermal analysis STA449F$_3$ Jupiter thermal analyser system in a dynamic atmosphere of N$_2$ at a heating rate of 10 °C/min.

X-ray crystallography

Diffraction intensities of **1-2** were measured with an Oxford Diffraction XCalibur Eos instrument equipped with Mo Kα radiation (λ = 0.71073 Å, 50 kV, 40 mA) at ambient temperature. Data collection and reduction were performed with the Oxford diffraction Crysalis system. The data of **3** was collected on a Bruker D8 Quest diffractometer equipped with a Photon 100 CMOS area detector system, using MoKα radiation with graphite monochromator (λ = 0.71073 Å) at T = 100(2) K The structure was solved by direct methods (SIR92)[25] and refined on F^2 by full-matrix least-squares methods using SHELXL-97.[26-27] Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\sum w(Fo^2 - Fc^2)^2]$ $(w = 1 / [\sigma^2 (Fo^2) + (aP)^2 + bP])$, where $P = (\mathrm{Max}(Fo^2,0) + 2Fc^2) / 3$ with $\sigma^2(Fo^2)$ from counting statistics. The function $R1$ and $wR2$ were $(\sigma||Fo| - |Fc||) / \sigma|Fo|$ and $[\sigma w (Fo^2 - Fc^2)^2 / \sigma(wFo^4)]^{1/2}$, respectively. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC 1402231-1402233. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: + (44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

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