Electronic Supporting Information (ESI) to the article

DFT Calculations in the Assignment of Solid-state NMR and Crystal Structure Elucidation of a Lanthanum(III) Complex with Dithiocarbamate and Phenantroline

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Table S1. Experimental (δ_{expt})[a] and ADF calculated (δ_{calc})[b] NMR ^{1}H and ^{13}C chemical shifts and coordination shifts (Δ_{coord})[c] (values within parenthesis) for the title complex (in ppm).

Label [d]	$\boldsymbol{\delta_{calc}}$(complex)	$\boldsymbol{\delta_{expt}}$(complex)
	^{13}C chemical shifts	
C13/C18/C23 (Dtc)	203.5	206.0
C1/C12	151.5	151.2 (+0.6)[e]
C5/C9	147.6	145.8 (-0.8)[e]
C3/C10	136.3	138.3 (+2.1)[e]
C4/C8	130.9	129.7 (+0.8)[e]
C6/C7	129.9	127.1 (+0.3)[e]
C2/C11	125.2	123.8 (+0.5)[e]
-CH_2	48.5	46.4
-CH_3	9.2	12.5
	^{1}H chemical shifts	
H1/H12	10.8	9.84 (+0.63)[e]
H3/H10	8.6	8.38 (+0.11)[e]
H6/H7	8.3	7.86 (+0.05)[e]
H2/H11	8.0	7.72 (+0.08)[e]
-CH_2	4.3	3.89
-CH_3	1.2	1.15

[a] ^{1}H and ^{13}C solution NMR experiments (in $CDCl_3$) were recorded in a 600 MHz spectrometer using TMS as an internal reference at 298 K.

[b] The experimental structure was fully optimised using conductor-like screening model (COSMO) at the DFT/PBE/TZ2P theory level in ADF2014 program. COSMO solvation model ($CDCl_3$) provides more realistic geometries than those from vacuum optimisation. The chemical shifts in optimized geometry were calculated at SO-ZORA/PBE/TZ2P level of theory. The shielding references for TMS (σ_{TMS}: ^{1}H = 31.4 ppm and ^{13}C = 185.6 ppm) were calculated at the same level of theory.

[c] $\Delta_{coord} = \delta_{expt}$ (complex) $-\delta_{expt}$ (PHEN) in ppm.

[d] For labels see Figure S1.

[e] versus δ_{expt}(PHEN) in ppm: C1/C12 = 150.6; C5/C9 = 146.6; C3/C10 = 136.2; C4/C8 = 128.9; C6/C7 = 126.8; C2/C11 = 123.3; H1/H12 = 9.21; H3/H10 = 8.27; H6/H7 = 7.81; H2/H11 = 7.64 (at 298K in $CDCl_3$ solution).

Table S2. Selected experimental X-ray crystallography (Expt.) and CASTEP calculated (3A/3B) bond lengths (Å) for the tris(*N*,*N*-diethyldithiocarbamato)(PHEN)lanthanum(III) complex.

Bond	Expt.	CASTEP	Bond	Expt.	CASTEP
C11-N11	1.326(11)	1.3498	C21-N21	1.324(11)	1.3481
C12-N12	1.337(11)	1.3541	C22-N22	1.339(11)	1.3561
C31A-N31A	1.339(9)	1.3570	C32-N23	1.349(11)	1.3544
C31B-N31B	1.365(2)	1.3574			
C11-S111	1.721(9)	1.7265	C21-S211	1.700(9)	1.7213
C11-S112	1.732(9)	1.7259	C21-S212	1.741(9)	1.7258
C12-S121	1.729(9)	1.7226	C22-S221	1.722(10)	1.7236
C12-S122	1.719(9)	1.7256	C22-S222	1.733(10)	1.7238
C31A-S131	1.693(9)	1.7236	C32-S231	1.725(8)	1.7211
C31A-S132	1.697(11)	1.7162	C32-S232	1.710(8)	1.7205
C31B-S131	1.692(9)	1.7236	N24-La1	2.709(7)	2.7360
C31B-S133	1.789(9)	1.7125	N25-La1	2.712(7)	2.7338
N14-La1	2.701(7)	2.7080			
N15-La1	2.732(6)	2.7311			
N11-C111	1.483(11)	1.4692	N21-C211	1.506(15)	1.4654
N11-C113	1.471(12)	1.4658	N21-C213	1.459(12)	1.4670
N12-C121	1.457(12)	1.4646	N22-C221	1.474(13)	1.4659
N12-C123	1.475(11)	1.4668	N22-C223	1.472(13)	1.4689
N31A-C131	1.356(9)	1.4661	N23-C231	1.482(11)	1.4710
N31A-C135	1.349(9)	1.4720	N23-C233	1.489(14)	1.4709
N31B-C133	1.378(10)	1.4683			
N31B-C137	1.379(10)	1.4726			
S111-La1	2.946(2)	2.9819	S211-La2	2.936(3)	2.9707
S112-La1	2.926(2)	2.9465	S212-La2	2.934(2)	2.9564
S121-La1	2.927(2)	2.9379	S221-La2	2.947(2)	2.9750
S122-La1	2.988(2)	3.0296	S222-La2	2.934(2)	2.9732
S131-La1	2.973(3)	3.0199	S231-La2	2.966(2)	3.0011
S132-La1	3.012(4)	2.9913	S232-La2	2.958(2)	2.9916
S133-La1	2.961(5)	3.0015			
C111-C112	1.506(14)	1.5178	C211-C212	1.40(2)	1.5197
C113-C114	1.499(15)	1.5196	C213-C214	1.498(16)	1.5164
C121-C122	1.516(15)	1.5217	C221-C222	1.531(18)	1.5258
C123-C124	1.514(15)	1.5208	C223-C224	1.503(17)	1.5217
C131-C132	1.44(3)	1.5222	C231-C232	1.473(14)	1.5231
C135-C136	1.46(3)	1.5226	C233-C234	1.484(17)	1.5229
C133-C134	1.59(3)	1.5193			
C137-C138	1.59(3)	1.5194			

Table S3. Selected experimental X-ray crystallography (Expt.) and CASTEP calculated (3A/3B) bond angles (°) for the tris(*N*,*N*-diethyldithiocarbamato)(1,10-PHEN)lanthanum(III) complex.

Bond	Expt.	CASTEP	Bond	Expt.	CASTEP
S111-C11-S112	118.6(5)	119.28	S211-C21-S212	118.0(5)	119.95
S121-C12-S122	118.7(5)	119.92	S221-C22-S222	120.3(5)	120.62
S131-C31A-S132	117.3(5	119.17	S231-C32-S232	119.1(5)	119.08
S131-C31B-S133	113.1(5)	119.60			
N11-C11-S111	121.7(7)	121.07	N21-C21-S211	120.2(7)	120.08
N11-C11-S112	119.7(7)	119.68	N21-C21-S212	121.8(7)	119.97
N12-C12-S121	119.4(7)	119.45	N22-C22-S221	120.3(7)	119.49
N12-C12-S122	121.9(7)	121.16	N22-C22-S222	119.3(8)	119.89
N31A-C31A-S131	122.0(9)	119.80	N23-C32-S231	120.5(6)	120.44
N31A-C31A-S132	116.1(9)	121.02	N23-C32-S232	120.4(6)	120.48
N31B-C31B-S131	121.7(7)	119.70	N14-La1-N15	60.1(19)	60.41
N31B-C31B-S133	120.0(4)	120.80	N24-La2-N25	60.8(2)	61.01
C11-S111-La1	86.1(3)	85.24	C22-S221-La2	88.1(3)	88.60
C11-S112-La1	86.5(3)	86.38	C22-S222-La2	88.3(3)	88.66
C12-S121-La1	91.4(3)	91.90	C21-S211-La2	91.1(3)	89.39
C12-S122-La1	89.6(3)	88.79	C21-S212-La2	90.4(3)	89.78
C31A-S131-La1	92.0(3)	90.06	C32-S231-La2	89.5(3)	85.20
C31A-S132-La1	90.5(4)	91.17	C32-S232-La2	90.0(3)	105.49
C31B-S133-La1	90.5(3)	90.60			
C11-N11-C111	122.4(8)	122.32	C21-N21-C211	123.3(9)	122.93
C11-N11-C113	122.2(8)	122.75	C21-N21-C213	122.6(8)	121.80
C111-N11-C113	115.4(8)	114.88	C211-N21-C213	113.7(8)	115.26
C12-N12-C121	122.6(8)	123.20	C22-N22-C221	121.9(9)	121.20
C12-N12-C123	122.8(8)	121.52	C22-N22-C223	121.2(9)	121.59
C121-N12-C123	114.5(7)	115.16	C221-N22-C223	116.8(8)	117.14
C31A-N31A-C131	132.5(15)	121.53	C32-N23-C231	120.9(7)	121.39
C31A-N31A-C135	126.1(14)	121.85	C32-N23-C233	122.4(8)	121.22
C131-N31A-C135	93.10(13)	116.42	C231-N23-C233	116.6(8)	117.39
N31A-C131-C132	106.7(17)	113.86	C31B-N31B-C133	119.0(7)	121.06
N31A-C135-C136	110.9(19)	114.53	C31B-N31B-C137	117.1(7)	121.23
			C133-N31B-C137	120.1(7)	117.78

Table S4. GIPAW/PBE calculated ^{13}C and ^{15}N nuclear shielding constants (in ppm) for geometry-optimised structures. A and B denote the two different configurations; 1A and 1B = all protons relaxed; 2A = all protons and C31A, N31A, S132, C131, C132, C135, C136 relaxed; 2B = all protons and C31B, N31B, S133, C133, C134, C137, C138 relaxed; 3A and 3B = all atoms relaxed.

Atom Label	1A	1B	2A	2B	3A	3B
C31	-47.2	-67.1	-34.3	-36.2	-37.6	-37.5
C32	-33.9	-33.9	-33.9	-34.1	-35.9	-36.0
C12	-32.3	-32.8	-32.7	-32.4	-35.2	-35.2
C22	-31.0	-31.2	-31.1	-31.2	-33.5	-33.6
C21	-27.8	-27.7	-27.8	-27.7	-32.8	-32.9
C11	-26.4	-27.0	-26.5	-27.0	-30.4	-30.0
C241	15.6	15.9	15.4	15.7	16.2	16.2
C251	17.8	17.8	17.7	17.6	16.7	16.8
C141	18.0	18.7	18.3	18.9	17.7	17.0
C251	20.1	18.8	19.2	19.8	18.9	18.6
C145	22.3	22.0	22.0	22.0	22.3	22.4
C245	22.7	22.3	22.7	22.4	24.6	22.5
C255	23.0	23.2	22.8	23.1	26.9	23.0
C155	24.9	24.9	25.0	25.0	27.3	24.7
C253	29.1	27.9	30.3	27.4	28.2	26.3
C253	30.4	29.3	29.6	29.6	28.8	28.0
C154	32.7	32.7	32.8	32.8	31.6	28.8
C246	32.9	32.8	33.0	32.9	35.2	32.0
C254	39.6	39.3	40.0	39.6	39.0	36.0
C144	39.6	39.6	39.7	39.6	39.1	38.6
C256	39.6	39.8	39.9	40.1	39.1	39.0
C244	40.2	40.3	40.6	40.6	39.3	39.2
C156	40.9	40.6	40.9	40.8	39.5	39.4
C242	41.5	41.6	41.4	41.4	39.5	39.5
C156	42.0	42.1	42.1	42.1	40.6	40.4
C242	43.2	42.4	42.7	42.1	40.8	40.6
C156	43.4	43.4	43.4	43.5	41.9	41.7
C152	45.5	46.0	46.1	46.1	43.1	42.8
C142	46.2	46.2	46.2	46.2	43.3	43.4
C252	46.5	46.9	46.6	46.8	46.8	46.6
C137	104.2	109.3	118.5	118.7	119.1	117.1
C133	107.7	111.6	119.0	119.1	119.8	117.4
C231	118.8	118.8	119.9	120.4	120.9	119.1
C233	118.9	118.9	119.0	116.0	121.4	120.4
C223	119.6	119.8	120.8	118.2	121.5	121.6
C221	120.6	121.3	120.5	121.7	122.7	122.2
C211	121.8	121.7	122.0	122.0	123.7	122.6
C213	123.2	123.2	123.2	123.2	124.8	125.1
C111	123.6	123.9	123.4	123.7	125.9	125.7
C123	127.1	127.0	127.2	127.2	127.6	126.1
C113	127.6	128.0	127.7	128.2	128.3	127.6
C121	129.8	130.4	130.3	130.4	129.5	127.9
C138	150.3	153.4	153.3	157.6	155.7	157.6
C134	151.3	155.0	157.1	160.6	156.4	157.8

C222	158.6	159.0	159.2	159.5	157.7	158.4
C224	159.8	159.7	157.6	159.9	158.2	159.7
C112	160.7	160.5	160.7	160.6	158.7	160.1
C124	161.5	160.7	160.8	163.8	159.4	160.1
C212	161.8	161.5	161.6	161.5	159.4	160.2
C232	161.8	161.7	161.7	161.7	160.0	160.8
C122	162.3	162.4	162.6	162.5	160.8	161.1
C232	162.5	162.5	161.8	162.5	161.1	161.4
C234	162.7	162.6	162.7	162.6	161.5	162.8
C114	164.8	164.8	164.6	164.7	161.6	163.2
N24	-70.5	-69.6	-70.8	-69.5	-72-0	-72.2
N25	-68.9	-65.0	-68.4	-68.7	-72.0	-72.3
N14	-64.4	-64.4	-64.9	-66.1	-66.7	-67.0
N15	-62.0	-62.5	-62.5	-62.4	-61.5	-60.8
N11	44.2	45.0	44.7	45.6	44.0	44.0
N12	40.4	40.4	40.8	40.8	45.2	45.2
N21	47.8	49.1	49.4	48.9	47.0	47.5
N22	48.3	48.9	47.5	48.2	47.4	47.2
N23	45.0	44.9	44.2	44.7	48.8	48.8
N31	76.1	43.3	54.7	53.3	53.6	53.4

Notes 1. Topological analysis of the electron density

QTAIM Bond concepts:
A chemical bond exists between two neighbouring atoms if there is a minimum in the density along the line connecting the local maxima, also called the *bond path*, of the electron density (***ρ***) that corresponds to the atomic positions. The hypothetical point along the *bond path* at the interatomic surface where the shared electron density (***ρ***) reaches a minimum is called as a *bond critical point (*BCrP*)*. The critical points that are found within ring structures are known as *ring critical points* (RCrPs). The value of electron density (***ρ***) at the BCrP measures the amount of ***ρ*** that built up in the bonding region. Therefore, high value of a BCrP may indicate predominantly covalent bond whereas the predominantly ionic bonds may have low values of BCrP and BCrP= 0 for a pure ionic bond.

Notes 2. Natural Bond Orbital (NBO) Analysis

The NBO search program (see Table S5) yielded the best Lewis structure (of lowest overall non-Lewis (NL) occupancy, 7.84e) with 89 core (CR), 85 bond (BD), and 14 lone pair (LP) "Lewis-type" (L) NBOs, which described about 97.98% of the total electron density. The residual 2.02% "delocalisation error" (corresponding to 7.84e) is primarily associated with valence-NL orbitals of BD* (valence antibond) orbitals.

Table S5. Output of Natural Bond Orbital (NBO) search program (25 cycles) for the best Lewis-like structure of the title lanthanum(III) complex.

Cycle No.	Occ. Thresh.	Occupancies		Lewis Structure				Low	High
		Lewis (L)	non-Lewis (NL)	CR	BD	nC	LP		
25	1.79	380.16	7.84	89	85	6	14	8	9

At cycle 25, the best Lewis structure (ground-state) of the title complex, with a strong delocalisation of the electron density, was accepted.

Orbital Type	L/NL	Electron contributions	% Electron Contribution
Core	Lewis	177.95	99.98
Valence	Lewis	202.21	96.29
Total	Lewis	380.16	97.98
Valence	non-Lewis	7.16	1.84
Rydberg	non-Lewis	0.68	0.18
Total	non-Lewis	7.84	2.02

NBOs: "CR" for a core, "LP" for a 1-center valence lone pair, "BD" for a 2-center bond, and "nC" for a n-center bond.

Table S6. Second order perturbation theory analysis of Fock matrix in NBO basis (only NBOs with E(2) > 0.5 kcal/mol are shown for some selected donor LPs (S211, N24) and BDs (La-S, S-C, and S-N)).

Donor (L)	Acceptor (NL)	Occupancy	E(2) kcal/mol
92. LP(1) S211	241. BD*(1) C211-N21	1.92841/0.04112	0.61
92. LP(1) S211	280. BD*(1) C21-S212	1.92841/0.05310	6.28
92. LP(1) S211	281. BD*(1) S211-La	1.92841/0.08680	8.30
92. LP(1) S211	282. BD*(1) S212-La	1.92841/0.10211	1.73
92. LP(1) S211	283. BD*(1) S221-La	1.92841/0.09310	1.66
92. LP(1) S211	284. BD*(1) S222-La	1.92841/0.08908	0.63
92. LP (1) S211	285. BD*(1) S231-La	1.92841/0.09112	0.62
93. LP (2) S211	278. BD*(2) C21-N21	1.59572/0.58512	58.06
93. LP (2) S211	279. BD*(1) C21-S211	1.59572/0.04718	1.33
93. LP (2) S211	281. BD*(1) S211-La	1.59572/0.08680	0.81
93. LP (2) S211	284. BD*(1) S222-La	1.59572/0.08908	3.06
93. LP (2) S211	286. BD*(1) S232-La	1.59572/0.08256	1.15
94. LP (1) S212	279. BD*(1) C21-S211	1.93709/0.04748	5.43
94. LP (1) S212	281. BD*(1) S211-La	1.93709/0.08680	1.95
94. LP (1) S212	282. BD*(1) S212-La	1.93709/0.10211	5.20
94. LP (1) S212	283. BD*(1) S221-La	1.93709/0.09310	2.03
94. LP (1) S212	285. BD*(1) S231-La	1.93709/0.09112	3.83
95. LP (2) S212	278. BD*(2) C21-N21	1.66904/0.58512	47.91
95. LP (2) S212	283. BD*(1) S221-La	1.66904/0.09310	1.31
95. LP (2) S212	285. BD*(1) S231-La	1.66904/0.09112	1.74
178. BD (1) C213-N21	277. BD*(1) C21-N21	1.97056/0.08150	1.27
178. BD (1) C213-N21	279. BD*(1) C21-S211	1.97056/0.04748	4.43
179. BD (1) C21-N21	241. BD*(1) C211N21	1.99002/0.04112	1.44
179. BD (1) C21-N21	276. BD*(1) C213-N21	1.99002/0.05427	1.02
179. BD (1) C21-N21	279. BD*(1) C21-S211	1.99002/0.04748	0.56
179. BD (1) C21-N21	280. BD*(1) C21-S212	1.99002/0.05310	0.52
179. BD (1) C21-N21	281. BD*(1) S211-La	1.99002/0.08680	1.91
179. BD (1) C21-N21	282. BD*(1) S212-La	1.99002/0.10211	1.81
180. BD (2) C21-N21	240. BD*(1) C211-C212	1.95076/0.01465	3.48
180. BD (2) C21-N21	275. BD*(1) C213-C17	1.95076/0.00921	1.84
180. BD (2) C21-N21	278. BD*(2) C21-N21	1.95076/0.58512	1.71
181. BD (1) C21-S211	276. BD*(1) C213-N21	1.97107/0.05427	7.22
181. BD (1) C21-S211	277. BD*(1) C21-N21	1.97107/0.08150	0.86
181. BD (1) C21-S211	283. BD*(1) S221-La	1.97107/0.09310	0.88
181. BD (1) C21-S211	284. BD*(1) S222-La	1.97107/0.08908	0.79
181. BD (1) C21-S211	285. BD*(1) S231-La	1.97107/0.09112	0.73
181. BD (1) C21-S211	286. BD*(1) S232-La	1.97107/0.08256	0.55
182. BD (1) C21-S212	241. BD*(1) C211N21	1.97077/0.04112	7.26
182. BD (1) C21-S212	277. BD*(1) C21-N21	1.97077/0.08150	0.76
182. BD (1) C21-S212	284. BD*(1) S222-La	1.97077/0.08908	0.74
183. BD (1) S211-La	277. BD*(1) C21-N21	1.93632/0.08150	9.91
183. BD (1) S211-La	280. BD*(1) C21-S212	1.93632/0.05310	0.67
183. BD (1) S211-La	281. BD*(1) S211-La	1.93632/0.08680	4.12
183. BD (1) S211-La	282. BD*(1) S212-La	1.93632/0.10211	6.64
183. BD (1) S211-La	283. BD*(1) S221-La	1.93632/0.09310	6.50
183. BD (1) S211-La	284. BD*(1) S222-La	1.93632/0.08908	6.73

183. BD (1) S211-La	285. BD*(1) S231-La	1.93632/0.09112	5.72
183. BD (1) S211-La	286. BD*(1) S232-La	1.93632/0.08256	4.04
184. BD (1) S212-La	277. BD*(1) C21-N21	1.93305/0.08150	10.27
184. BD (1) S212-La	281. BD*(1) S211-La	1.93305/0.08680	1.17
184. BD (1) S212-La	284. BD*(1) S222-La	1.93305/0.08908	2.08
184. BD (1) S212-La	285. BD*(1) S231-La	1.93305/0.09112	0.53
184. BD (1) S212-La	286. BD*(1) S232-La	1.93305/0.08256	1.38
90. LP (1) N24	281. BD*(1) S211-La	1.84608/0.08680	14.50
90. LP (1) N24	283. BD*(1) S221-La	1.84608/0.09310	16.09
90. LP (1) N24	284. BD*(1) S222-La	1.84608/0.08908	0.99
90. LP (1) N24	285. BD*(1) S231-La	1.84608/0.09112	9.26
152. BD (1) C241-C242	281. BD*(1) S211-La	1.98348/0.08680	0.70
152. BD (1) C241-C242	283. BD*(1) S221-La	1.98348/0.09310	1.01
153. BD (1) C241-N24	281. BD*(1) S211-La	1.98286/0.08680	0.71
153. BD (1) C241-N24	283. BD*(1) S221-La	1.98286/0.09310	1.21
156. BD (1) C244-C245	281. BD*(1) S211-La	1.97217/0.08680	0.65
158. BD (1) C244-C246	281. BD*(1) S211-La	1.97891/0.08680	1.36
159. BD (1) C245-N24	281. BD*(1) S211-La	1.97891/0.08680	2.95
159. BD (1) C245-N24	283. BD*(1) S221-La	1.97891/0.09310	2.11
159. BD (1) C245-N24	285. BD*(1) S231-La	1.97891/0.09112	0.85
162. BD (1) C253-C254	281. BD*(1) S211-La	1.98345/0.08680	0.76
162. BD (1) C253-C254	282. BD*(1) S212-La	1.98345/0.10211	0.91
166. BD (1) C246-C256	281. BD*(1) S211-La	1.97207/0.08680	0.74

“LP” for a 1-center valence lone pair, “BD” for a 2-center bonding, BD* for a 2-center anti-bond NBOs, the numbers in parenthesis denote the bond order between the pair of atoms.

Table S7. Natural Population Analysis (NPA) of some selected atoms (La, S, and N).

Atom No.	Natural Charge	Core	Valence	Rydberg	Total
La1	1.06292	53.98388	1.80251	0.15069	55.93708
S221	-0.21591	9.99904	6.19620	0.02067	16.21591
S222	-0.23656	9.99908	6.21595	0.02152	16.23656
S231	-0.20352	9.99907	6.18442	0.02003	16.20352
S232	-0.18377	9.99906	6.16265	0.02205	16.18377
S211	-0.27274	9.99905	6.25214	0.02155	16.27274
S212	-0.18413	9.99907	6.16256	0.02249	16.18413
N22	-0.38560	1.99924	5.37634	0.01001	7.38560
N23	-0.39221	1.99923	5.38287	0.01011	7.39221
N11	-0.38837	1.99924	5.37912	0.01000	7.38837
N24	-0.50004	1.99946	5.48992	0.01066	7.50004
N25	-0.49423	1.99947	5.48231	0.01245	7.49423

Table S8. Cartesian coordinates (in Å) of CASTEP/PBE optimised 3B structure of the title complex (used for NBO and AIM analysis).

Atom	X	Y	Z	Atom	X	Y	Z
1 La	4.871073	9.913694	5.033163	40 H	7.297494	12.311427	10.152013
2 S	2.741222	11.951052	5.108915	41 H	6.243690	12.882157	8.850036
3 S	2.092825	9.231028	4.068611	42 H	8.181433	14.097935	7.807958
4 S	5.964840	12.284682	6.408408	43 H	9.249478	13.526153	9.110467
5 S	7.618018	9.819233	6.151880	44 H	7.897174	14.627665	9.477519
6 S	6.300450	8.483984	2.818437	45 H	9.380871	11.204798	9.406556
7 S	5.661101	11.365725	2.527847	46 H	9.155056	10.006682	8.116643
8 N	0.362311	11.272150	4.115801	47 H	8.807086	8.966254	10.379092
9 N	7.646172	11.431716	8.295645	48 H	7.318968	8.918126	9.424120
10 N	7.029462	9.952820	0.715120	49 H	7.502020	10.121088	10.722194
11 N	4.523915	7.286688	5.647340	50 H	-1.614882	10.634092	3.960039
12 N	4.494968	9.169113	7.656986	51 H	-0.394410	9.361607	3.798955
13 C	1.620561	10.858040	4.392376	52 H	-1.455299	9.885530	1.577487
14 C	-0.639678	10.390953	3.513510	53 H	0.290986	10.249798	1.560101
15 C	-0.675464	10.530564	1.998470	54 H	-0.899583	11.564873	1.703267
16 C	-0.091187	12.634795	4.413842	55 H	-0.816708	12.912168	3.634678
17 C	-0.726691	12.738481	5.792280	56 H	0.764906	13.314429	4.327623
18 C	7.138406	11.202773	7.066404	57 H	-1.616317	12.101001	5.874951
19 C	7.275442	12.606767	9.094323	58 H	-1.017693	13.775985	5.999312
20 C	8.210289	13.779374	8.856600	59 H	-0.009398	12.437554	6.565412
21 C	8.642897	10.554135	8.916208	60 H	4.460355	6.756047	3.657208
22 C	8.030093	9.590221	9.918725	61 H	4.228615	4.298782	4.091319
23 C	6.386066	9.942410	1.910299	62 H	4.178596	3.489783	6.446018
24 C	7.202379	11.199373	-0.041335	63 H	4.167337	4.027274	8.870793
25 C	6.016803	11.582407	-0.916475	64 H	4.449058	11.117967	8.340883
26 C	7.615667	8.723401	0.155230	65 H	4.390279	10.510185	10.759803
27 C	6.613669	7.804161	-0.522636	66 H	4.327940	8.078445	11.396866
28 C	4.424912	6.371654	4.677288	67 H	4.228333	5.716040	10.682810
29 C	4.301211	5.000539	4.920511	68 H	8.101962	11.070143	-0.657464
30 C	4.280706	4.553278	6.223020	69 H	7.400282	11.999773	0.686026
31 C	4.354395	5.484772	7.276630	70 H	5.757870	10.771928	-1.608888
32 C	4.466640	6.862042	6.941688	71 H	6.263596	12.477451	-1.506702
33 C	4.282924	5.088203	8.644779	72 H	5.137510	11.803520	-0.299283
34 C	4.314925	6.017454	9.638957	73 H	8.110648	8.189773	0.979454
35 C	4.404971	7.410478	9.340739	74 H	8.388420	9.036494	-0.559004
36 C	4.472706	7.845414	7.991750	75 H	7.127687	6.918912	-0.920733
37 C	4.385981	8.392900	10.351594	76 H	6.114235	8.292808	-1.366730
38 C	4.403114	9.724502	10.003170	77 H	5.856069	7.468465	0.193194
39 C	4.444701	10.069654	8.645843				

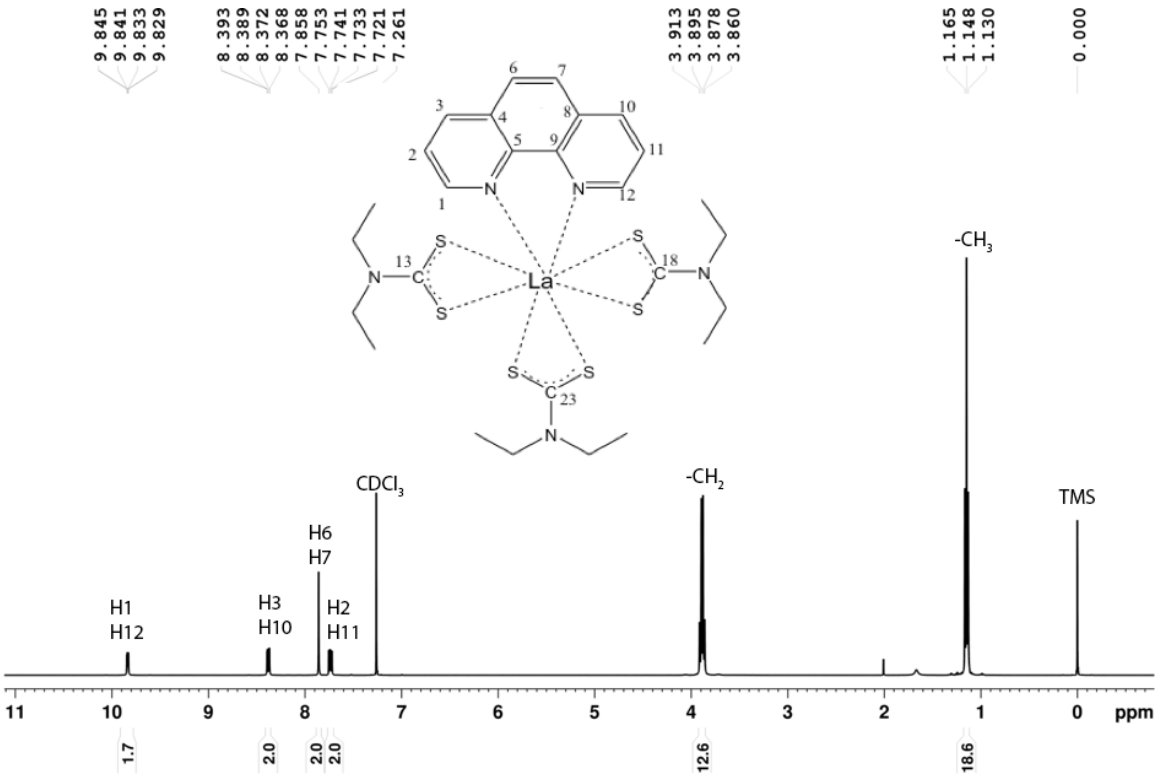
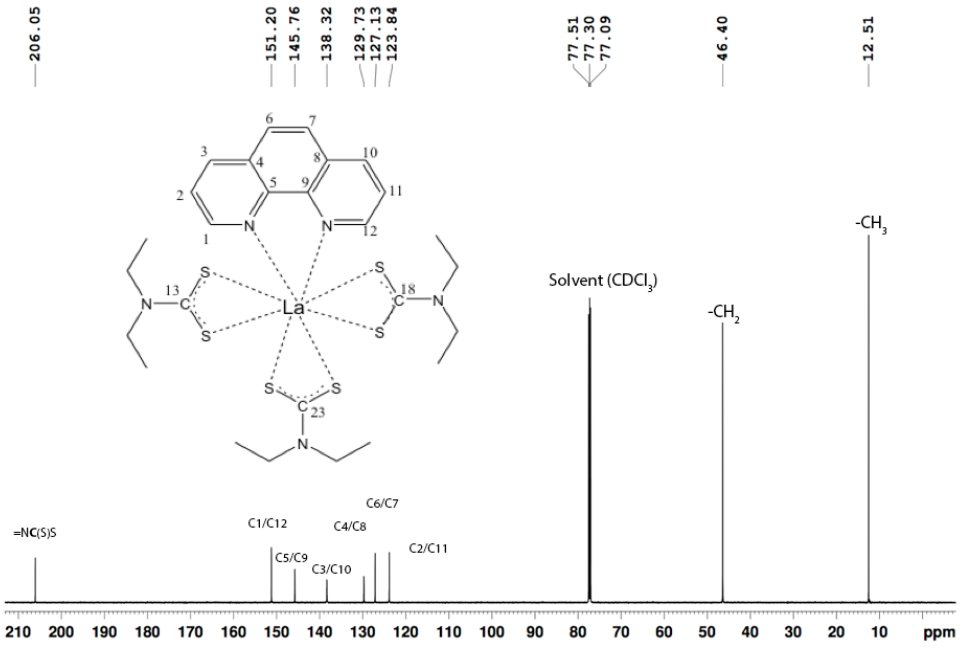


Figure S1. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum for the tris(*N*,*N*-diethyldithio-carbamato)(1,10-PHEN)lanthanum(III) complex. (32 transients, 2s relaxation delay, 32k time domain (TD) points, internal reference = TMS).

a)



b)

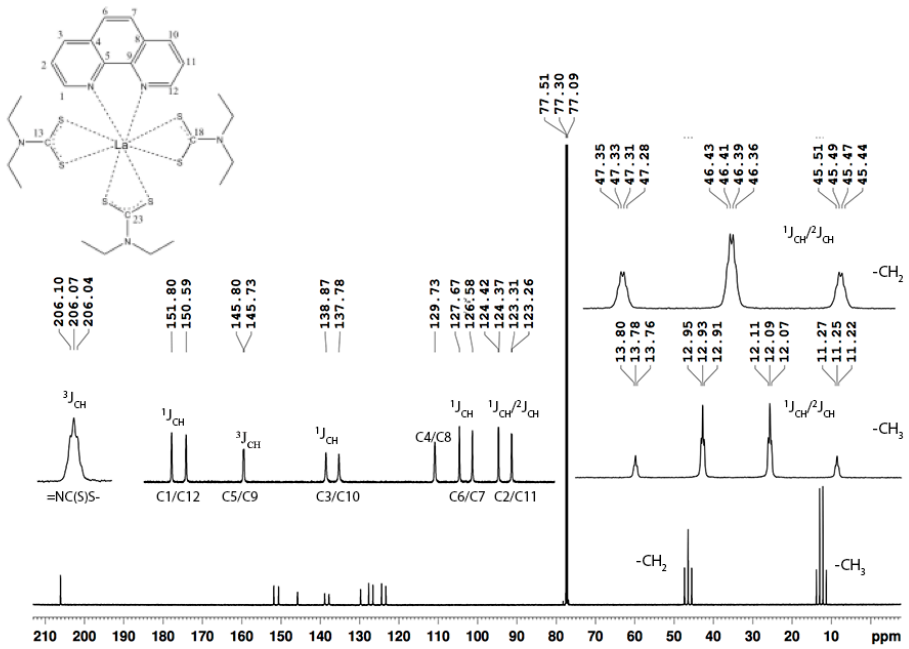
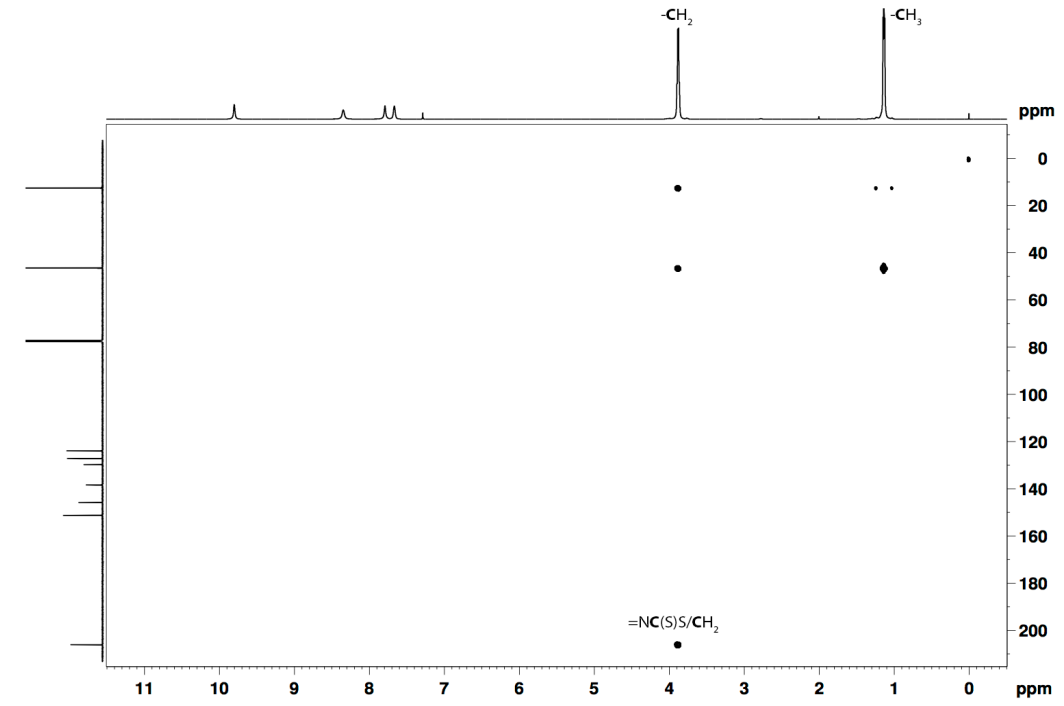


Figure S2. ^{1}H (a) decoupled and (b) coupled ^{13}C NMR (150.8 MHz, $CDCl_3$) spectra for the tris(*N*,*N*-diethyldithiocarbamato)(1,10-PHEN)lanthanum(III) complex (internal reference = TMS).

a)



b)

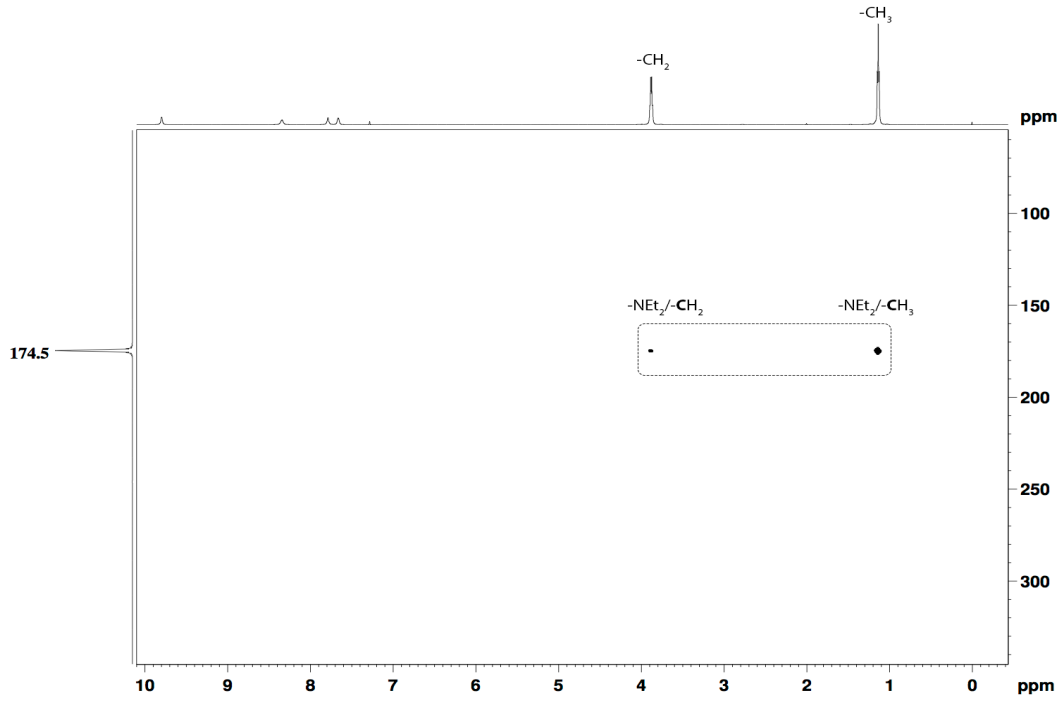
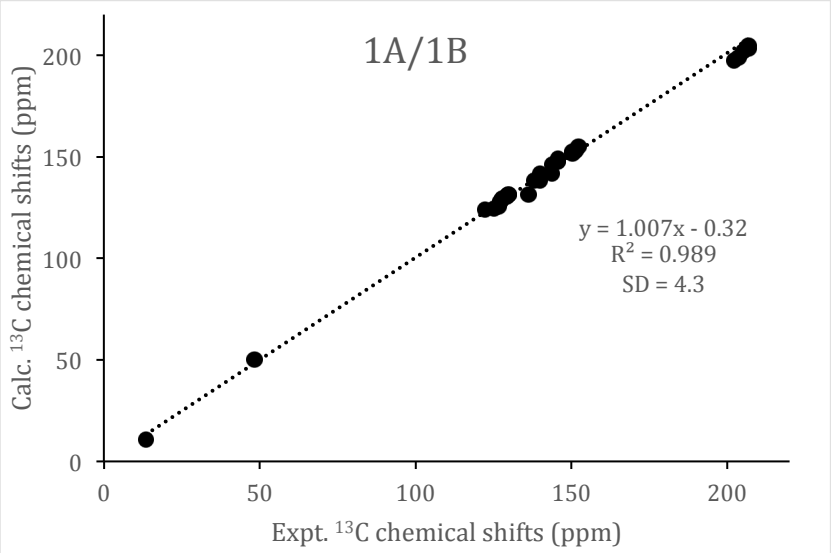
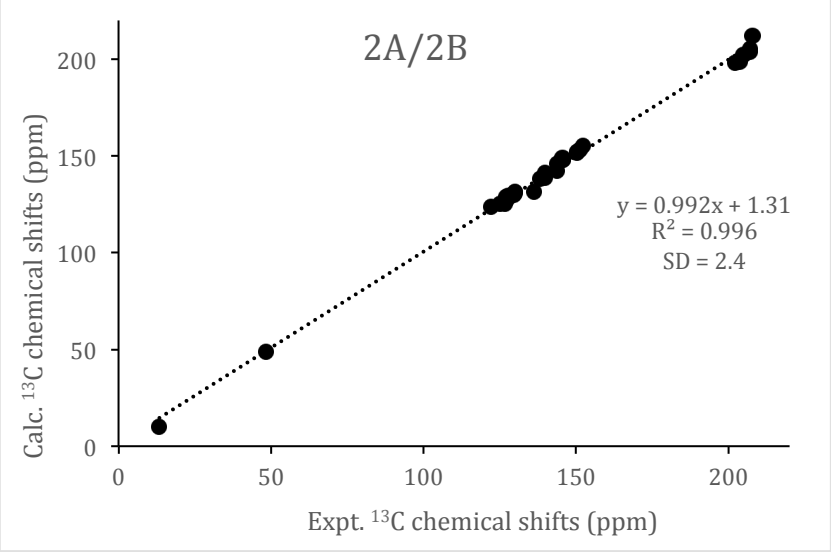


Figure S3. (**a**) ^{1}H-^{13}C and (**b**) ^{1}H-^{15}N HMBC NMR spectra (600 MHz, $CDCl_3$) of the tris(*N*,*N*-diethyldithiocarbamato)(1,10-PHEN)lanthanum(III) complex.

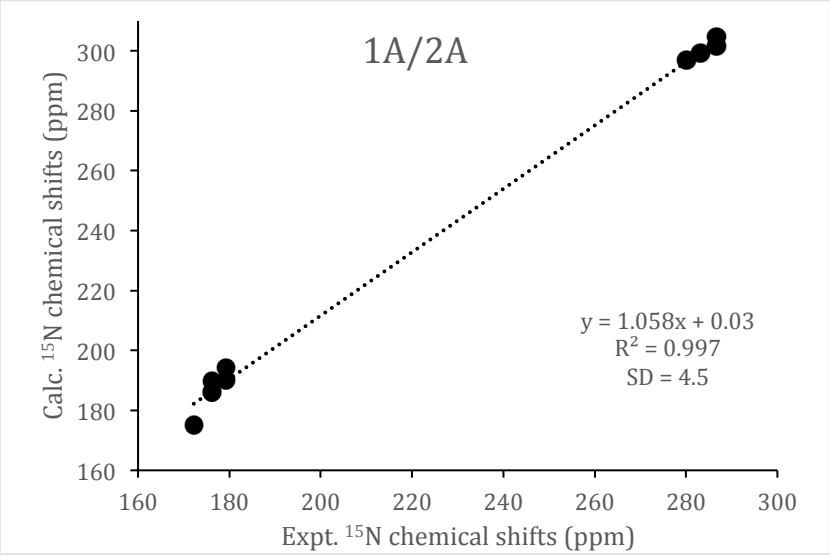
a)


1A/1B
y = 1.007x - 0.32
R² = 0.989
SD = 4.3
Calc. ¹³C chemical shifts (ppm)
Expt. ¹³C chemical shifts (ppm)
0
50
100
150
200

b)


2A/2B
y = 0.992x + 1.31
R² = 0.996
SD = 2.4
Calc. ¹³C chemical shifts (ppm)
Expt. ¹³C chemical shifts (ppm)
0
50
100
150
200

c)



d)

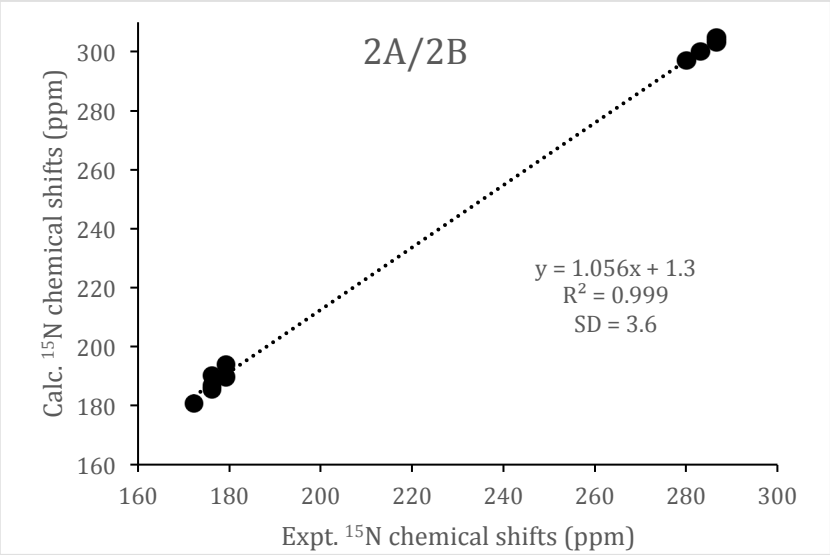


Figure S4. Experimental *vs*. computed chemical shift plots for the geometry-optimised structures of the title lanthanum complex. The GIPAW/PBE calculated ^{13}C (a) and (b), and ^{15}N (c) and (d) chemical shifts for the structures 1A/2A and 1B/2B, respectively. A and B denote the two different configurations; 1A and 1B = all protons relaxed; 2A = all protons and C31A, N31A, S132, C131, C132, C135, C136 relaxed; 2B = all protons and C31B, N31B, S133, C133, C134, C137, C138 relaxed. The standard deviation (SD) between the experimental and calculated chemical shift is also shown.

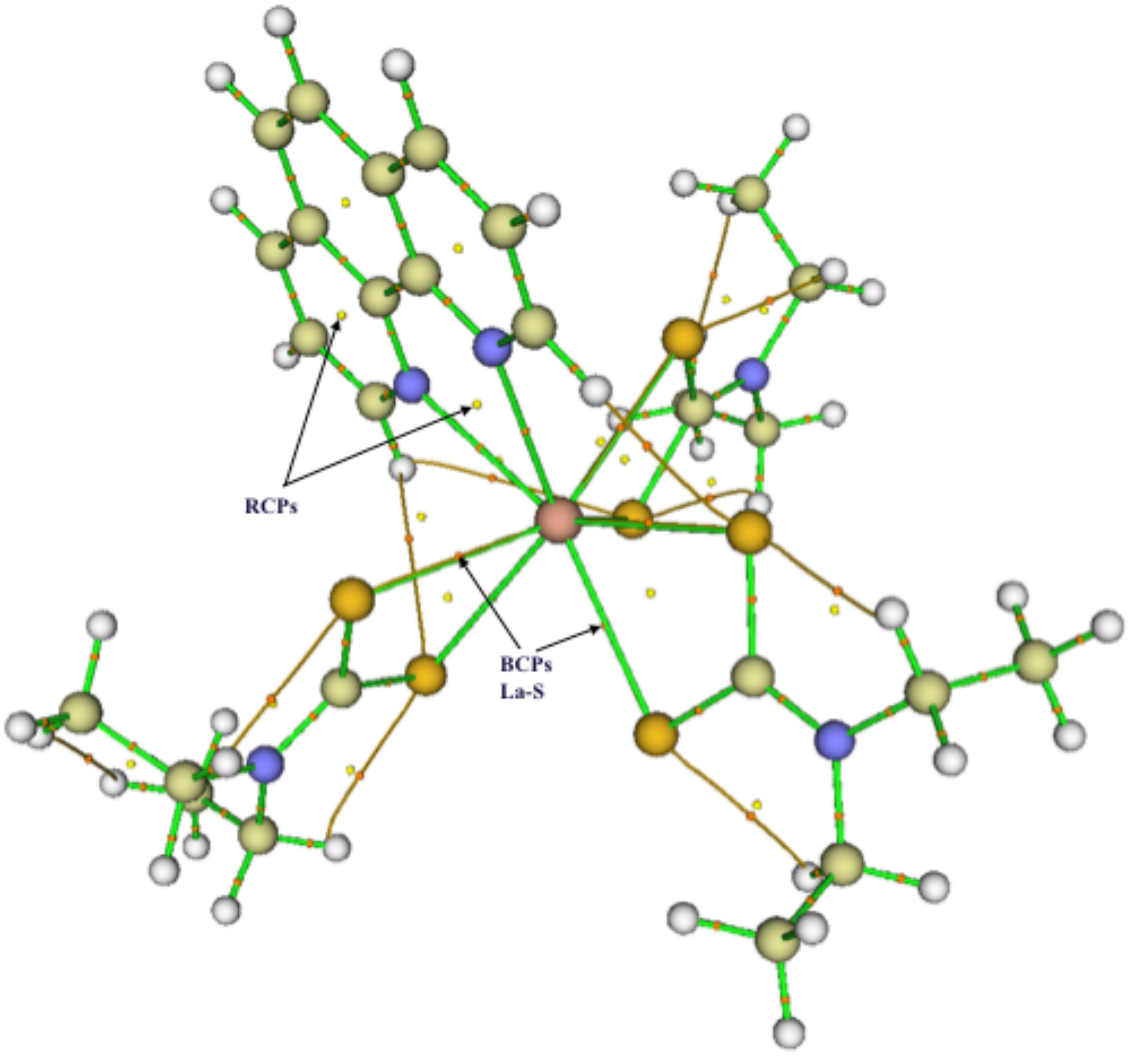
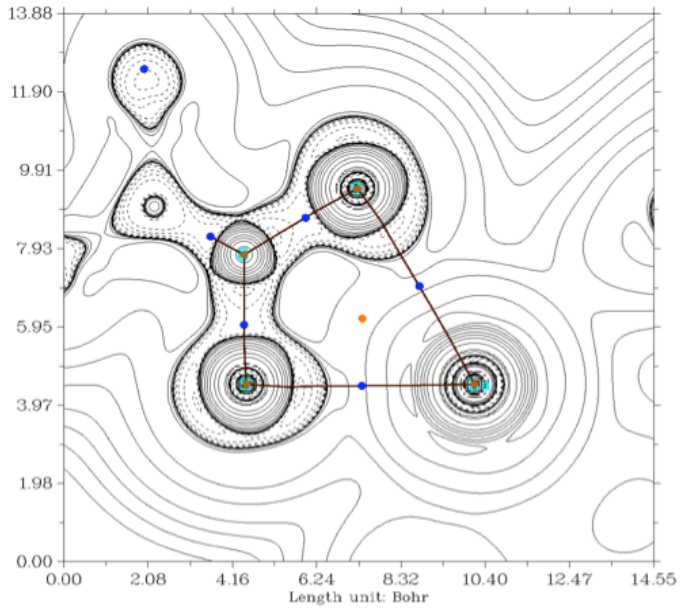


Figure S5. A molecular graph for the title lanthanum(III) complex. Nuclear critical points (NCrPs) are in grey (H), yellow-brown (C), blue (N), silver-brown (S), and red-brown (La); bond critical points (BCrPs) in orange; ring critical points (RCrPs) in yellow.

a)



b)

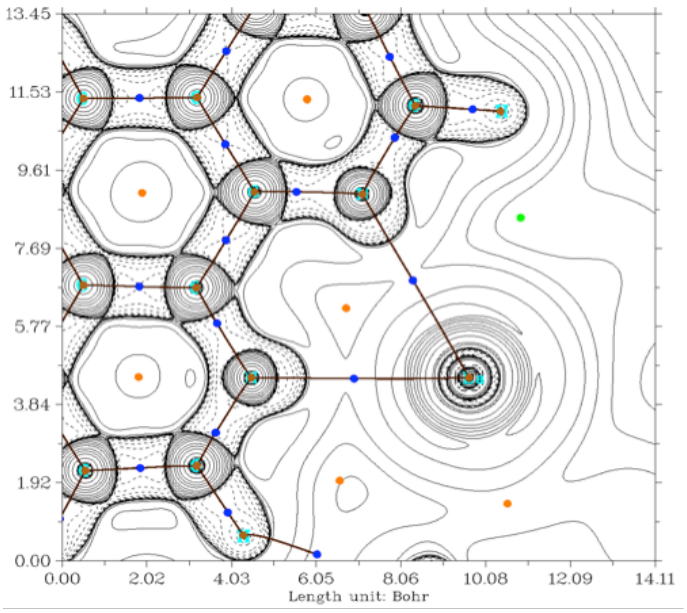


Figure S6. Contour plot representations of the Laplacian of the electron density (∇^2_ρ) in the plane spanned by the atoms of (**a**) La-Dtc (plane S-La-S) and (**b**) La-PHEN (plane N-La-N) groups, showing bond paths (BPs, brown line), bond critical points (BCrPs, blue), and ring critical points (RCrPs, orange). Black (solid) and dash lines depict negative, while solid-grey lines depict positive values, respectively.

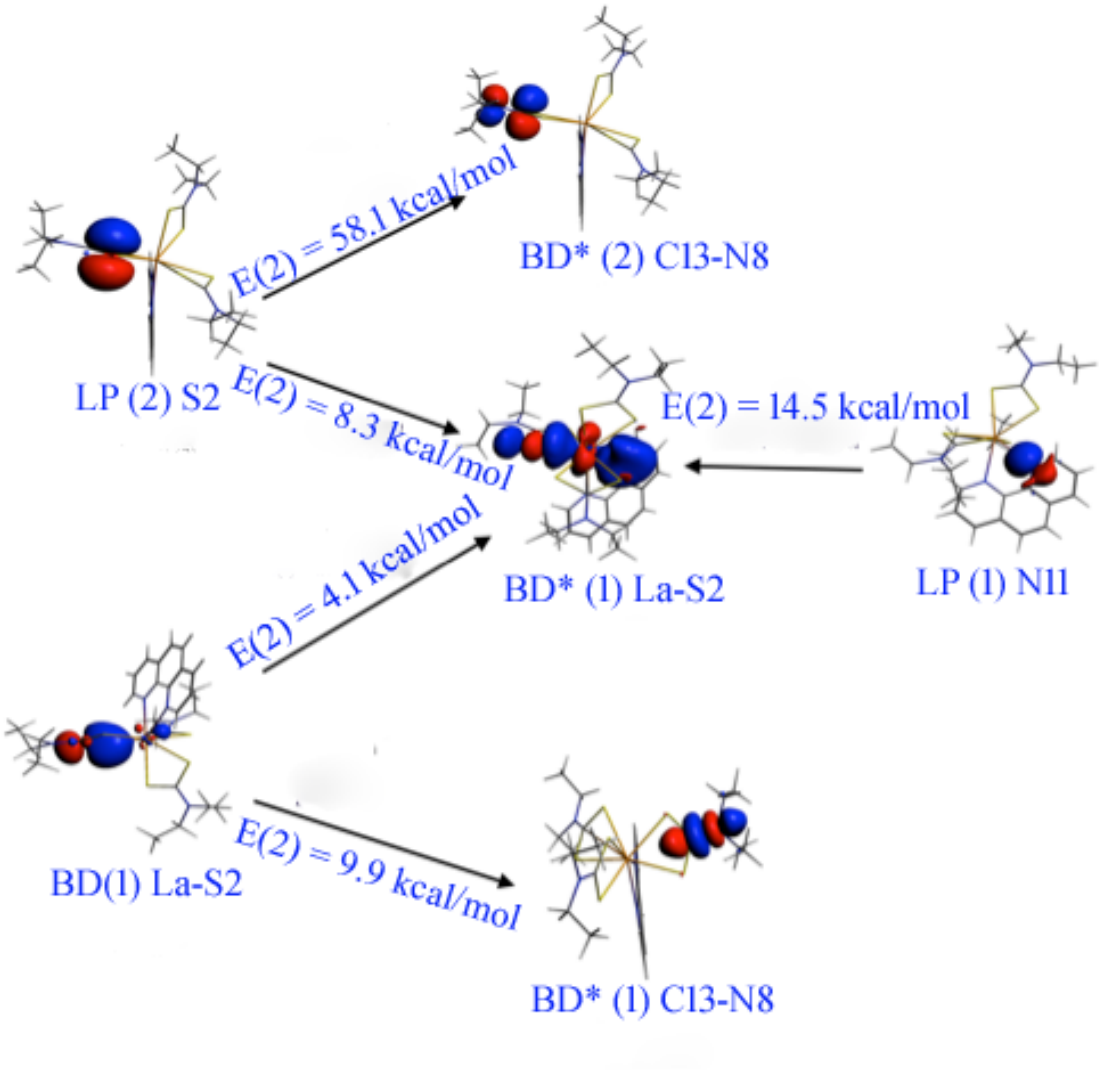


Figure S7. Visualisation of some selected donor-acceptor NBOs. The stabilisation energy, E(2) in kcal/mol, associated with the donor-acceptor interaction (estimated via the second-order perturbation theory) is also shown. LP = lone pair, BD = 2-center bond, and BD* = anti-bonding NBOs.

HOMO-LUMO analysis (Figure S8):

The LUMO and LUMO+1 orbitals are concentrated on the PHEN ligand. The greater contributions of the LUMO orbitals come from 3-center NL (3Cn and 3C*) NBOs of the PHEN 'C' and 'N' atoms. On the other hand, the HOMO and HOMO-1 levels show greater contributions of LPs of S atoms and La-S bonding NBOs.

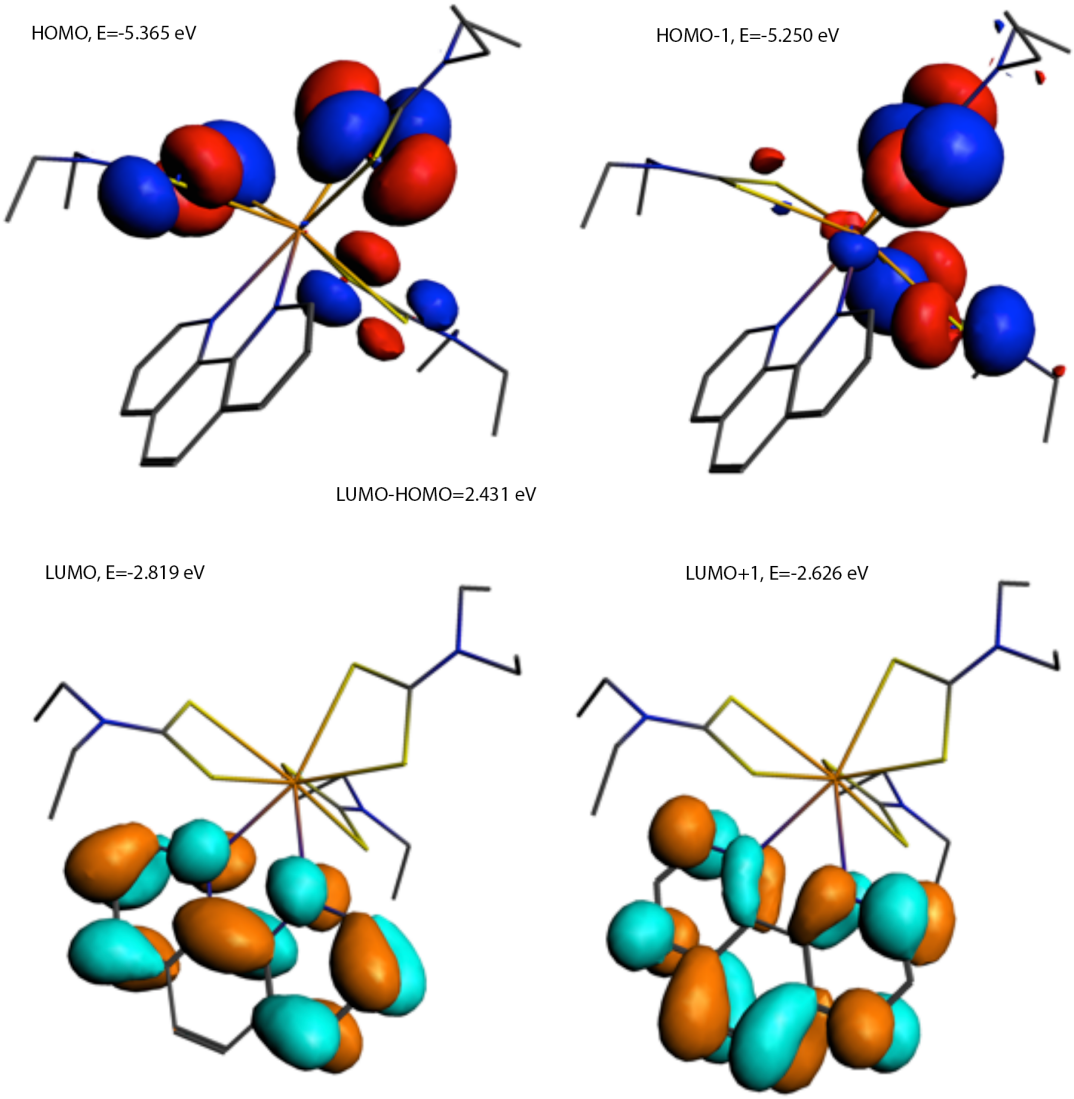


Figure S8. Plots of the frontier orbitals of the tris(*N*,*N*-diethyldithiocarbamato)(PHEN)- lanthanum(III) complex by B3LYP/TZ2P theory. Orbital plots were prepared with the 'adfview' tool of the ADF graphical user interface. HOMO-LUMO gap is 2.431 eV.