Supplementary information

Ln$_3$I$_5$(S$_2$N$_2$)(S$_2$)(THF)$_{10}$– a new type of molecular compounds

A.A. Fagin[a], G.K. Fukin[a], A.V. Cherkasov[a], A.F. Shestakov[b], A.P. Pushkarev[a], T.V. Balashova[a],

A.A.Maleev[a] and M.N. Bochkarev[a]*

[a] *G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, 603950 Tropinina 49,*

*Nizhny Novgorod, Russian Federation. *e-mail: mboch@iomc.ras.ru*

[b] *Institute of Problems of Chemical Physics of Russian Academy of Sciences, Academician Semenov avenue 1,*

142432 Chernogolovka, Russian Federation.

Supporting Information Contents

X-ray structure characterization

The unit cell in **1** and **2** (Fig. 1, S1) (unlike complex **3** (Fig. S2)) contains two crystallographically independent molecules. The geometrical parameters of the independent molecules close to each other except the Nd(2)-N(2) distances which is 2.523(7) Å in one of the independent molecules of complex **1** but 2.460(8) Å in the other molecule. The geometrical parameters of S$_2$N$_2$ and S$_2$ ligands in **1-3** (Table S1) are close to literature data[1-5] and reflect their dianione nature. The S$_2$N$_2$ ligand in **1-3** shows a wide spectrum of coordination possibilities. The M(1) atoms are coordinated bidentately by the single S(1)-N(1) bond of S$_2$N$_2$ ligand. Towards the M(2) and M(3) atoms the S$_2$N$_2$ ligand acts as chelate and bridge ones respectively. From this viewpoint the S$_2$N$_2$ ligand is a central fragment in the molecules of complexes **1-3**. In spite of difference in coordination environment of Ln atoms in **1-3** the Ln(1,2,3)-N(1,2) distances vary in narrow limit of values in all the cases.

Table S1. Selected bond lengths (Å) in the molecules Ln$_3$I$_5$(S$_2$N$_2$)(S$_2$)(solv.)$_{10}$

Bond	Compound		
	1	**2**	**3**
M(1)-I(1)	3.1045(9)	3.1086(8)	3.140(1)
M(1)-I(2)	3.1106(8)	3.1178(8)	3.135(1)
M(1)-S(1)	2.856(2)	2.861(3)	2.889(3)
M(1)-N(1)	2.488(8)	2.458(9)	2.453(9)

M(2)-I(3)	3.2067(9)	3.2142(9)	3.221(1)
M(2)-I(4)	3.1812(9)	3.1865(9)	3.197(1)
M(2)-S(1)	2.890(2)	2.896(3)	2.943(3)
M(2)-N(2)	2.460(8)	2.493(8)	2.507(9)
M(2)-S(3)	2.839(3)	2.805(3)	2.826(3)
M(2)-S(4)	2.798(3)	2.834(2)	2.854(3)
M(3)-I(5)	3.1524(8)	3.1576(8)	3.174(1)
M(3)-N(2)	2.469(8)	2.482(8)	2.499(9)
M(3)-S(3)	2.771(2)	2.795(2)	2.822(3)
M(3)-S(4)	2.794(2)	2.787(2)	2.797(3)
S(1)-N(1)	1.684(8)	1.706(8)	1.699(9)
N(1)-S(2)	1.573(8)	1.561(9)	1.591(9)
S(2)-N(2)	1.531(8)	1.500(9)	1.52(1)
S(3)-S(4)	2.084(3)	2.091(4)	2.097(4)
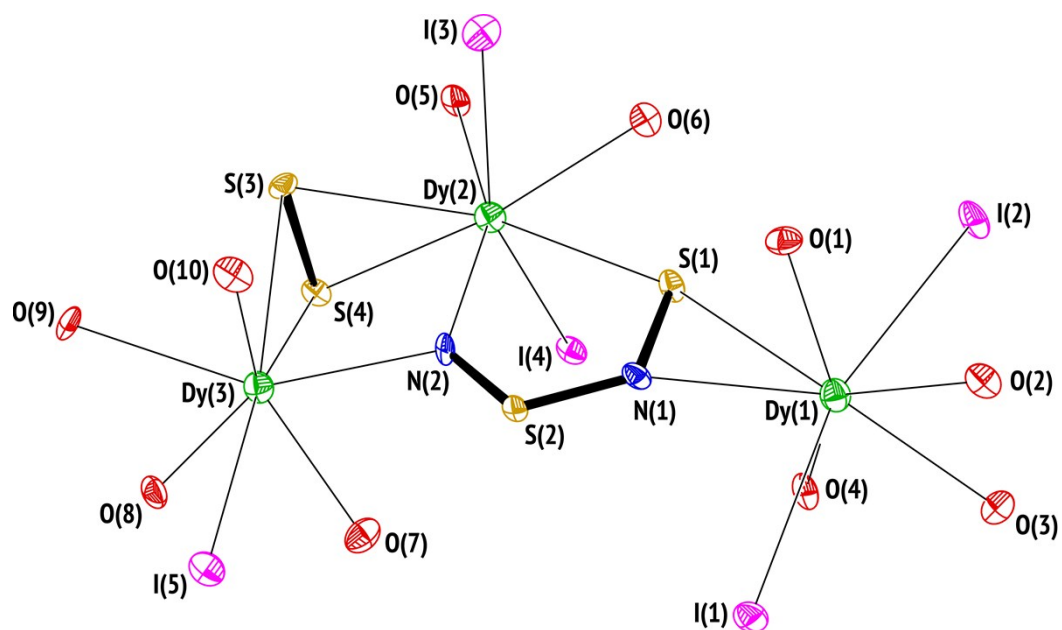
Fig. S1 Molecular structure of $Dy_3I_5(S_2N_2)(S_2)(THF)_{10}$ (**2**). Carbon and hydrogen atoms of THF are omitted for clarity.
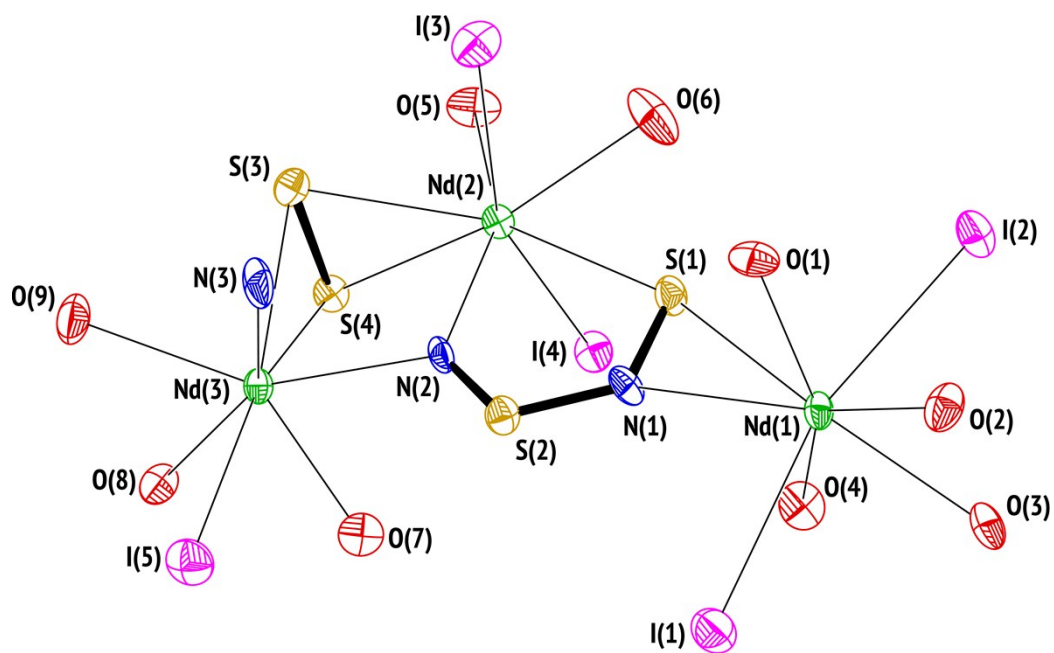
Fig. S2 Molecular structure of $Nd_3I_5(S_2N_2)(S_2)(THF)_9(i\text{-}PrNH_2)$ (**3**). Carbon and hydrogen atoms of $i\text{-}PrNH_2$ and THF ligands are omitted for clarity.

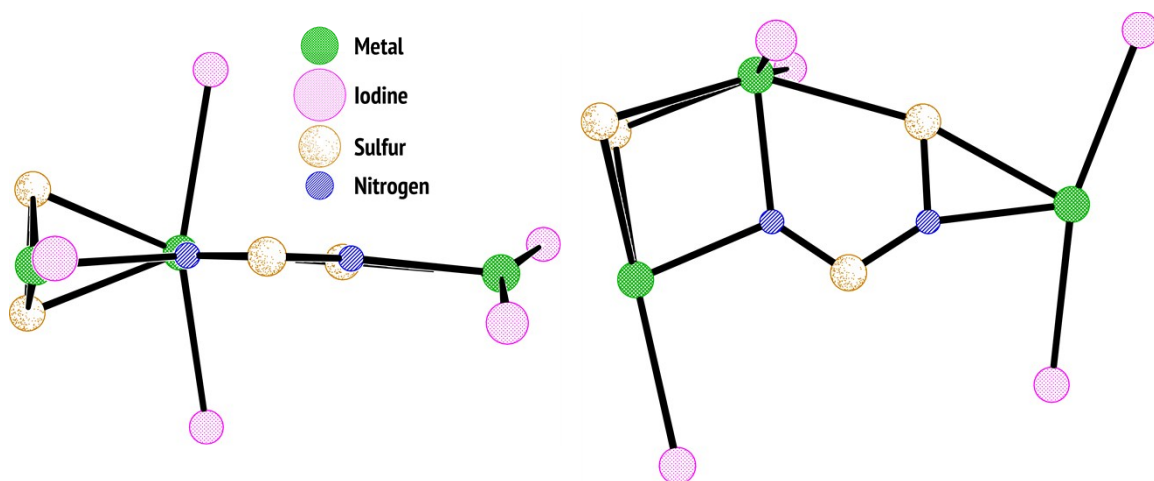**Fig. S3** View of inorganic framework of $Nd_3I_5(S_2N_2)(S_2)(THF)_{10}$ (**1**) molecule along the Nd(1)Nd(2)Nd(3) plane (left) and the I(5)Nd(3)S(3)S(4) plane (right).
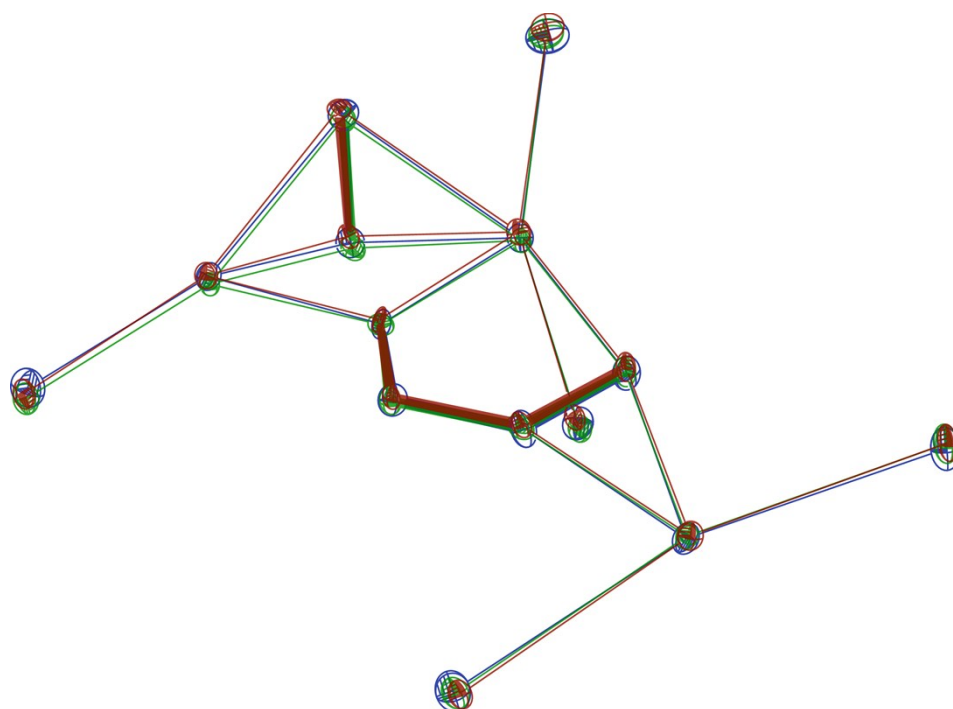
Fig. S4 Aligned inorganic frameworks of the complexes **1** (green), **2** (red) and **3** (blue).

The X-Ray data for **1-3** were collected on *Bruker D8 Quest* (**1**, **2**) and *Agilent Xcalibur E* (**3**) diffractometers (graphite-monochromated, *MoK$_\alpha$* radiation, ω-scans technique, λ = 0.71073 Å, *T* = 100(2) K*). The structures were solved by direct methods and were refined on *F²* using *SHELX / SHELXTL*[6,7] and *CrysAlis Pro*[8] packages. All non-hydrogen atoms were found from Fourier syntheses of electron density and were refined anisotropically. The unit cell in **1** and **2** contains two crystallographically independent molecules. Displacement parameters of most equivalent atoms of independent molecules were restrained with *EADP* instructions. All hydrogen atoms were placed in calculated positions and were refined in the riding model with U_{iso}(H) =1.2 U_{eq} of their parent atoms. Pseudo merohedral twinning was found in **1** and **2** using *PLATON / TwinRotMat*[9]. A batch scaling factor was introduced to describe the twin volume fractions in **1**–**3**, resulting in a 0.503 / 0.497 ratio for the volume of domains in **1**, 0.434 / 0.363 / 0.115 / 0.088 for the volume of domains in **2** (including racemic twinning) and 0.982 / 0.018 ration for the volume of domains in **3**. *SADABS*[10] and *ABSPACK*[8] were used to perform area-detector scaling and absorption corrections. CCDC-1056902 (**1**), 1056903 (**2**), 1056904 (**3**) contain the supplementary crystallographic data (excluding structure factors) for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via ccdc.cam.ac.uk/getstructures.

Table S2. Main crystallographic data and structure refinement details for complexes **1-3**.

	1	2	3
Empirical formula	$C_{40}H_{80}I_5N_2Nd_3O_{10}S_4$, 2THF	$C_{40}H_{80}I_5N_2Dy_3O_{10}S_4$, 2THF	$C_{39.54}H_{80.77}I_5N_{2.57}Nd_3O_{9.44}S_4$, 2THF
Formula weight	2088.72	2143.50	2082.82
T, K	100		
Wavelenght, Å	0.71073		
Crystal system	Monoclinic		Orthorhombic
Space group	$P2(1)$		$P2(1)2(1)2(1)$
a, Å	12.393(1)	12.418(1)	12.5369(2)
b, Å	43.389(5)	43.476(5)	12.7379(2)
c, Å	12.684(1)	12.707(2)	43.8743(7)
α, °	90	90	90
β, °	90.013(2)	90.030(2)	90
γ, °	90	90	90
Volume, Å^3	6820(1)	6860(1)	7006.5(2)
Z	4	4	4
ρ_{calc}, Mg/m^3	2.034	2.075	1.975
Absorption coefficient, mm^{-1}	4.687	5.657	4.562
F(000)	4012	4084	4002
Crystal size, mm	$0.18 \times 0.09 \times 0.04$	$0.12 \times 0.10 \times 0.10$	$0.40 \times 0.40 \times 0.40$
θ range for data collection, °	2.47—29.00	2.34—27.00	2.94—26.00
Index ranges	$-16 \leq h \leq 16$ $-59 \leq k \leq 58$ $-17 \leq l \leq 17$	$-15 \leq h \leq 15$ $-55 \leq k \leq 55$ $-16 \leq l \leq 16$	$-15 \leq h \leq 15$ $-15 \leq k \leq 15$ $-54 \leq l \leq 54$
Reflections collected	75809	68257	104407
Independent reflections	35242	29695	13746
R_{int}	0.0585	0.0348	0.0866

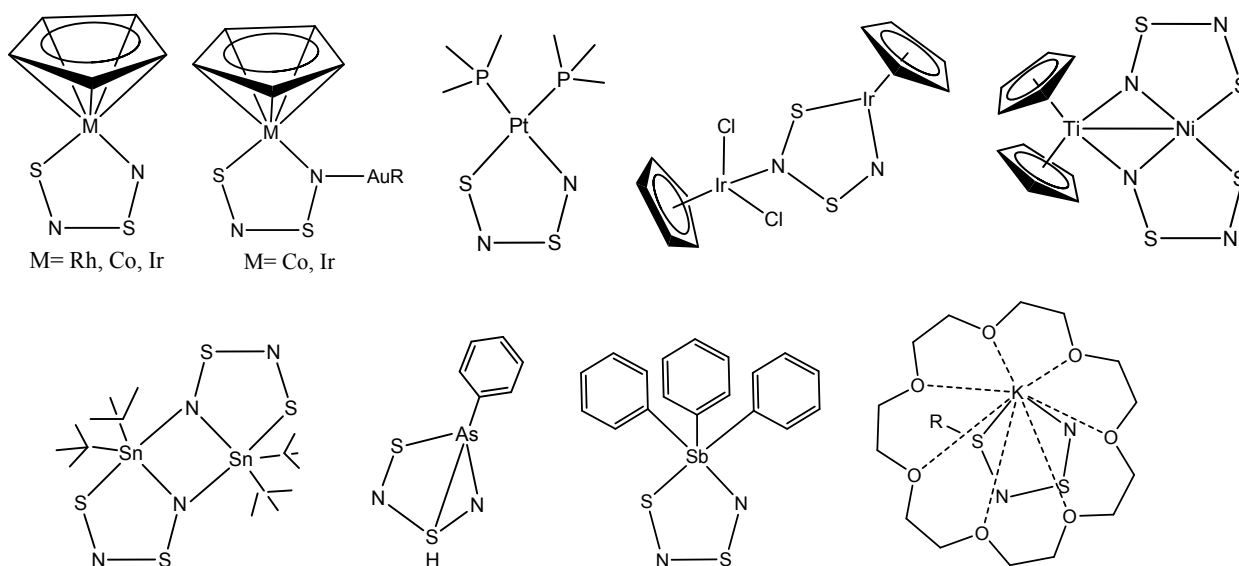|			
Completness to θ, %	99.9	99.8	99.8
Goodness-of-fit on F^2	1.009	1.085	1.188
Final R_1 indices (I > 2σ(I))	0.0450	0.0340	0.0540
R_2 indices (All Data)	0.0671	0.0851	0.1118
Largest diff. peak and hole, e/Å^3	1.478 / -1.199	1.853 / -1.600	1.582 / -1.395

Fig. S5. Types of known complexes with S_2N_2 ligands.

Computed molecular structures and calculations details

To calculate the structure (Fig. S6) and energy of **1**, **2** and **3** nonempirical PBE density functional method2[11] was used. All calculations were performed using the PRIRODA program package[12,13] in scalar-relativistic approximation, which is based on the full four-component one-electron Dirac equation with spin–orbit effects separated out[14]. This leads to four-component one-electron wave functions. The energy-optimized extended Gaussian basis set of double-polarized quality for large components, and the corresponding kinetically balanced basis for small components was used: Ln (30s,29p,20d,14f,6g)/[9s,8p,6d,3f,1g] S (15s,11p,3d)/[4s,3p,1d], C,N,O (10s,7p,3d)/[3s,2p,1d], and H (6s,2p)/[2s,1p]. This basis is compatible with recently proposed basis Ln (23s,16p,12d,6f)/[18s,12p,9d,3f][15] for scalar relativistic calculation of

lanthanide complexes. The calculations were carried out at the Joint Supercomputer Center of Russian Academy of Sciences, Moscow, Russia.
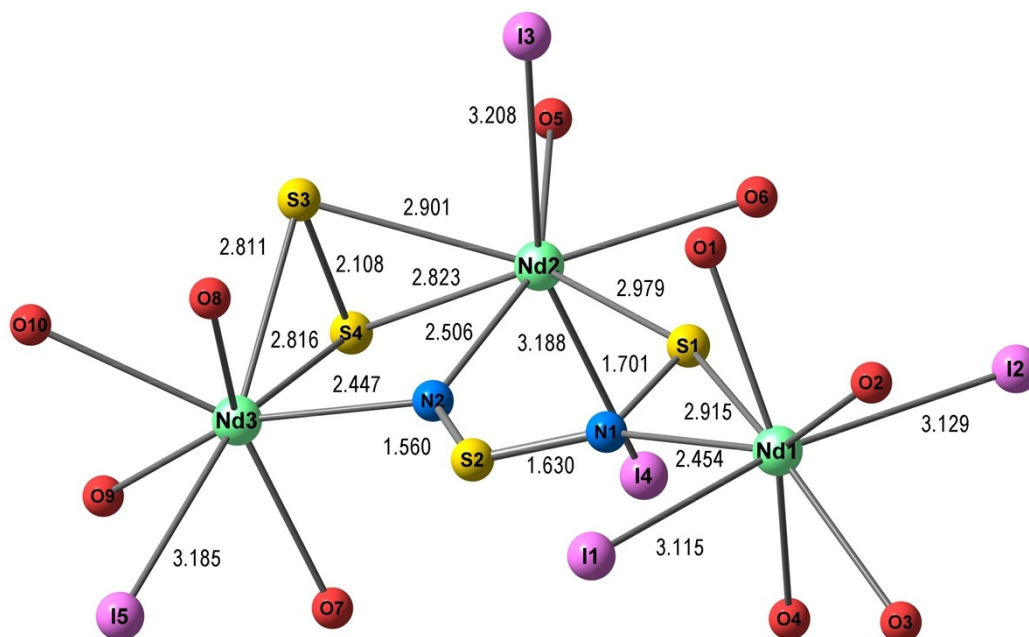

Fig. S6 Calculated molecular structure and bond lengths in $Nd_3I_5(S_2N_2)(S_2)(THF)_{10}$ (**1**).

Table S3. The charge (q) and spin density (s) on the selected atoms in the complexes **1**, **2** and **3**.

atom	1		2		3	
	q	s	q	s	q	s
Ln(1)	0.208	3.116	0.268	4.779	0.209	3.115
I(1)	-0.336	-0.034	-0.339	0.034	-0.334	-0.035
I(2)	-0.331	-0.033	-0.337	0.035	-0.330	-0.033
Ln(2)	0.142	3.100	0.204	4.854	0.141	3.096
I(3)	-0.347	-0.024	-0.333	0.053	-0.341	-0.028
I(4)	-0.335	-0.032	-0.329	0.061	-0.329	-0.024
Ln(3)	0.212	3.107	0.266	4.814	0.204	3.104
I(5)	-0.344	-0.018	-0.339	0.021	-0.339	-0.020
S(1)	-0.030	-0.034	-0.040	0.059	-0.031	-0.029
N(1)	-0.127	-0.013	-0.128	0.031	-0.127	-0.008
S(2)	0.255	0.004	0.248	0.001	0.248	0.003
N(2)	-0.240	-0.018	-0.247	0.014	-0.241	-0.021
S(4)	-0.142	-0.058	-0.140	0.095	-0.139	-0.055

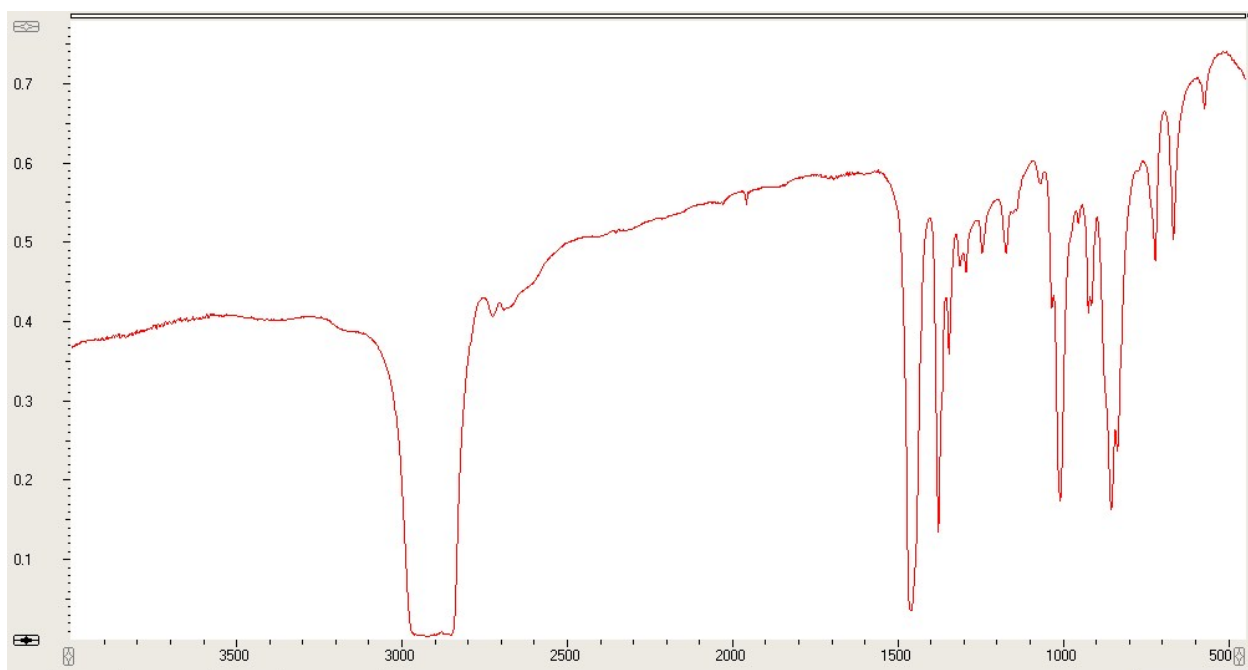|						
S(3)	-0.137	-0.054	-0.141	0.087	-0.140	-0.053

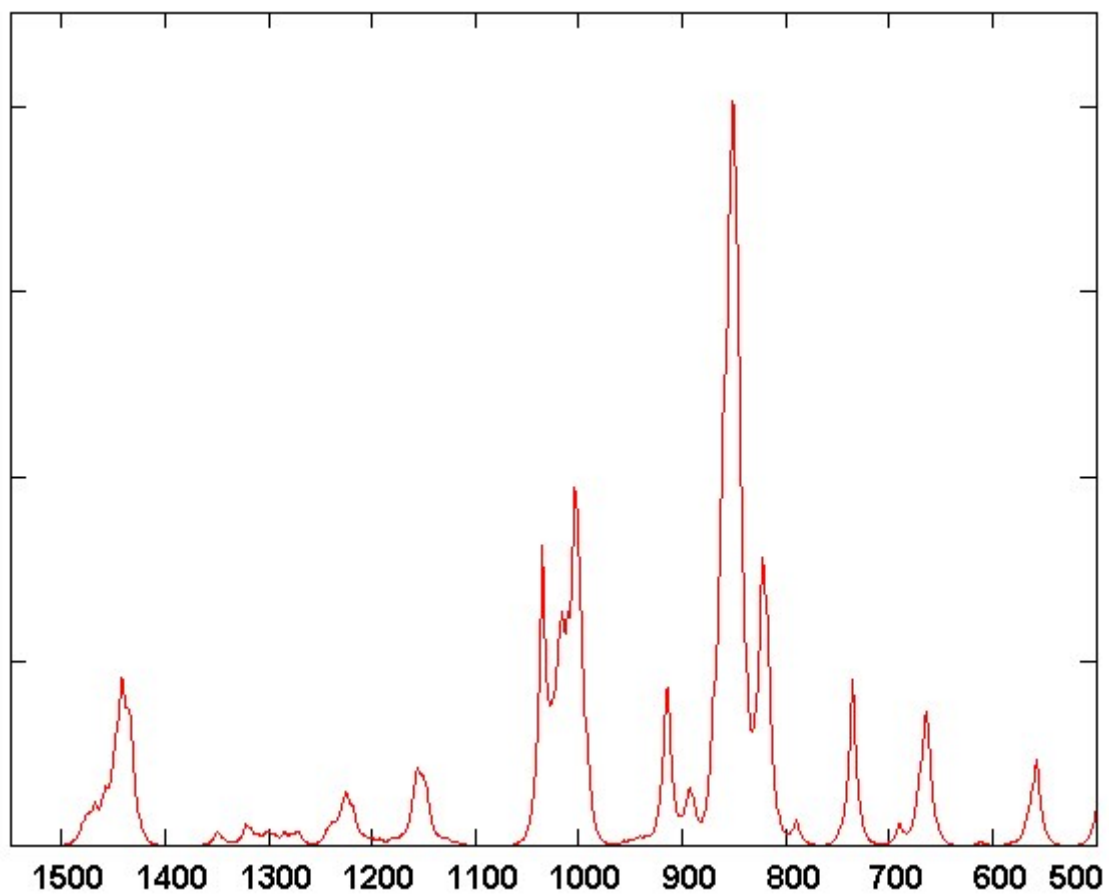**Fig. S7a.** IR spectra of **1** (Nujol mulls).

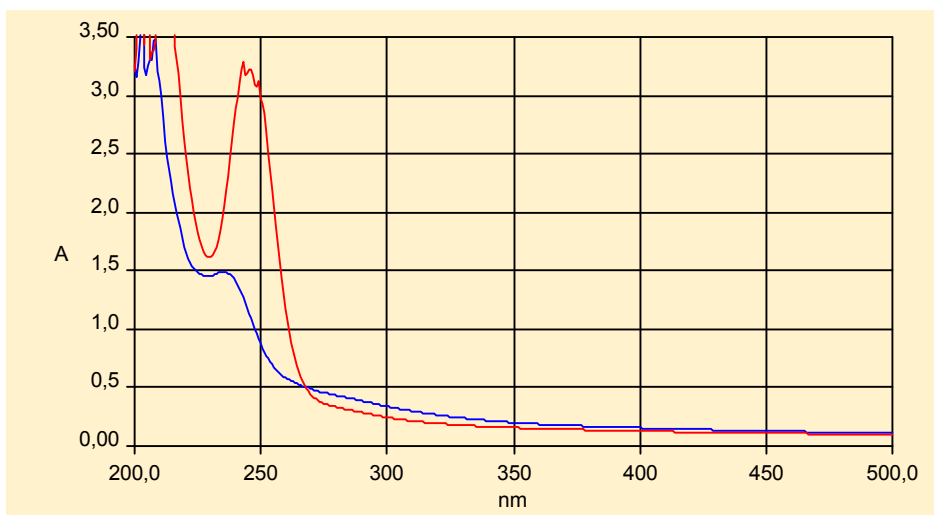**Fig. S7b.** Calculated IR spectra of **1.**

Fig. S8 Absorption spectra of **1** (red) and **2** (blue) in acetonitrile solution.

References

1. V. Matuska, et al. *Eur. J. Inorg. Chem.*, 2009, 4483—4490.

2. P. G. Waddell, A. M. Z. Slawin, N. Sieffert, M. Bühl and J. D. Woollins, *Eur. J. Inorg. Chem.*, 2010, 3185—3194.

3. A. M. Z. Slawin, P. G. Waddell and J. D. Woollins, *Acta Cryst.,* 2010, **E66**, M418.

4. Y. Li, et al. *Organometallics,* 2005, **24**, 1982-1988.

5. E. C. Brown, et al. *Inorg. Chem.* 2004, **43**, 3335−3337.

6. G. M. Sheldrick, SHELXTL v.6.12: Structure Determination Software Suite. *Bruker AXS, Madison, WI* , 2000.

7. G. M. Sheldrick, *Acta Cryst.,* 2008, **A64**, 112-122.

8. CrysAlis Pro, *Agilent Technologies Ltd*, Yarnton, England, 2011.

9. A. L. Spek, *Acta Cryst.,* 2009, **D65**, 148-155.

10. Sheldrick, G.M. SADABS v.2.01. Bruker/Siemens Area Detector Absorption Correction Program; *Bruker AXS*, Madison, WI, 1998.

11. J. P. Perdew, K. Burke and M. Ernzerhof, *Rev. Lett.,* 1996, **77**, 3865-3868.

12. D. N. Laikov, *Chem. Phys. Lett.,* 1997, **281**, 151-156.

13. D. N. Laikov, *Chem. Phys. Lett.,* 2005, **416**, 116-120.

14. K. G. Dyall, *J. Chem. Phys.,* 1994, **100**, 2118 - 2127.

15. D. A. Pantazis and F. Neese, *J. Chem. Theor. Comput.,* 2009, **5**, 2229 - 2238.