Electronic supplementary information (ESI)

Tetradentate selenium ligand as a building block for homodinuclear complexes of Pd(II) and Ru(II) having seven membered rings or bis-pincer coordination mode: high catalytic activity of Pd-complexes for Heck reaction

Dipanwita Das, Pradhumn Singh, Monika Singh[‡] and Ajai K. Singh*
Department of Chemistry, Indian Institute of Technology, Delhi, New Delhi110016, India

Table S1. Crystal data and structural refinements for **L**, **1**, **2** and **3**

	L (763938)	**1** (765901)	**2** (763939)	**3** (770943)
Empirical formula	$C_{34}H_{30}Se_4$	$C_{40}H_{40}Cl_2O_8Pd_2Se_4$	$C_{44}H_{38}B_2F_8N_2Pd_2Se_4$	$C_{46}H_{42}Cl_2F_{12}P_2Ru_2Se_4$
Crystal size [mm]	0.504 × 0.314 × 0.144	0.203 × 0.150 × 0.065	0.524 × 0.342 × 0.178	0.524× 0.324 × 0.184
θ range [°]	2.35 – 28.32	2.25 – 25.05	2.25 – 25.73	2.20 – 28.32
Index ranges	$-14 \le h \le 14$ $-12 \le k \le 12$ $-13 \le l \le 13$	$-13 \le h \le 13$ $-17 \le k \le 17$ $-18 \le l \le 18$	$-26 \le h \le 26$ $-12 \le k \le 12$ $-22 \le l \le 22$	$-34 \le h \le 34$ $-13 \le k \le 13$ $-22 \le l \le 22$
Max./min. Transmission	0.489/ 0.164	0.771/ 0.482	0.493/ 0.207	0.545/ 0.282
Data/restraints/ parameters	2596 / 0 / 172	8180 / 40 / 494	4042 / 1 / 280	4996 / 12/ 296
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0997$, $wR_2 = 0.1692$	$R_1 = 0.0610$, $wR_2 = 0.1391$	$R_1 = 0.0458$, $wR_2 = 0.1323$	$R_1 = 0.0836$, $wR_2 = 0.1650$
R indices (all data)	$R_1 = 0.1141$, $wR_2 = 0.1745$	$R_1 = 0.1071$, $wR_2 = 0.1579$	$R_1 = 0.0572$, $wR_2 = 0.1397$	$R_1 = 0.1493$, $wR_2 = 0.1923$
Largest diff. peak/hole [e.Å^{-3}]	0.891/ -0.861	1.209 / -0.668	1.220 / -0.676	0.848/ -0.682

Table S2. Bond Lengths and Bond Angles of **L**, **1**, **2** and **3**

	Bond Length [Å]		Bond Angle [°]	
L	Se(1)—C(5)	1.907(9)	C(5)– Se(1)–C(4)	103.5(4)
	Se(1)—C(4)	1.971(9)	C(12)–Se(2)–C(11)	98.6(4)
	Se(2)—C(12)	1.939(8)	C(3)–C(4)–Se(1)	104.2(6)
	Se(2)—C(11)	1.973(10)	C(6)–C(5)–Se(1)	124.5(7)
			C(10)–C(5)–Se(1)	116.2(7)
			C(2)–C(11)–Se(2)	112.1(7)
			C(17)–C(12)–Se(2)	121.7(7)
			C(13)–C(12)–Se(2)	117.0(7)
1	Pd(1)—C(2)	2.128(13)	C(2)–Pd(1)–C(3)	37.5(5)
	Pd(1)—C(3)	2.143(11)	C(2)–Pd(1)–C(1)	37.1(5)
	Pd(1)—C(1)	2.160(11)	C(3)–Pd(1)–C(1)	66.8(5)
	Pd(1)—Se(2)	2.4494(16)	C(2)–Pd(1)–Se(2)	125.9(4)
	Pd(1)—Se(1)	2.4557(17)	C(3)–Pd(1)–Se(2)	158.1(4)
	Se(1)—C(10)	1.943(10)	C(1)–Pd(1)–Se(2)	92.4(4)
	Se(1)—C(4)	2.022(11)	C(2)–Pd(1)–Se(1)	127.9(4)
	Se(2)—C(15)	1.922(10)	C(3)–Pd(1)–Se(1)	94.3(4)
	Se(2)—C(14)	1.994(10)	C(1)–Pd(1)–Se(1)	160.1(4)
			Se(2)–Pd(1)–Se(1)	105.54(5)
			C(10)–Se(1)–C(4)	92.3(5)
			C(10)–Se(1)–Pd(1)	111.5(3)
			C(4)–Se(1)–Pd(1)	102.3(3)
			C(15)–Se(2)–C(14)	97.7(4)
			C(15)–Se(2)–Pd(1)	104.2(3)
			C(14)–Se(2)–Pd(1)	109.0(3)
2	Pd(1)—C(9)	2.009(5)	C(9)–Pd(1)–N(1)	178.0(2)
	Pd(1)—N(1)	2.148(5)	C(9)–Pd(1)–Se(2)	86.09(15)
	Pd(1)—Se(2)	2.4005(8)	N(1)–Pd(1)–Se(2)	92.18(13)
	Pd(1)—Se(1)	2.4084(7)	C(9)–Pd(1)–Se(1)	85.97(15)
	Se(1)—C(6)	1.942(6)	N(1)–Pd(1)–Se(1)	95.75(13)
	Se(1)—C(7)	1.950(6)	Se(2)–Pd(1)–Se(1)	172.06(3)
	Se(2)—C(12)	1.931(7)	C(6)–Se(1)–C(7)	100.8(3)
	Se(2)—C(11)	1.954(6)	C(6)–Se(1)–Pd(1)	102.22(17)
			C(7)–Se(1)–Pd(1)	93.79(17)
			C(12)–Se(2)–C(11)	98.7(3)
			C(12)–Se(2)–Pd(1)	105.0(2)
			C(11)–Se(2)–Pd(1)	93.93(17)

3	Ru(1)—C(23)	2.139(15)	C(23)–Ru(1)–Cl(1)	130.2(9)
	Ru(1)—C(22)	2.176(16)	C(22)–Ru(1)–Cl(1)	163.6(5)
	Ru(1)—C(21)	2.177(19)	C(21)–Ru(1)–Cl(1)	139.6(7)
	Ru(1)—C(19)	2.19(2)	C(19)–Ru(1)–Cl(1)	89.2(7)
	Ru(1)—C(18)	2.20(2)	C(18)–Ru(1)–Cl(1)	95.1(11)
	Ru(1)—C(20)	2.215(16)	C(20)–Ru(1)–Cl(1)	104.9(7)
	Ru(1)—Cl(1)	2.394(4)	C(23)–Ru(1)–Se(1)	85.9(5)
	Ru(1)—Se(1)	2.4945(18)	C(22)–Ru(1)–Se(1)	100.0(5)
	Ru(1)—Se(2)	2.5164(18)	C(21)–Ru(1)–Se(1)	135.1(7)
	Se(1)—C(1)	1.923(11)	C(19)–Ru(1)–Se(1)	134.1(11)
	Se(1)—C(7)	1.966(13)	C(18)–Ru(1)–Se(1)	100.6(11)
	Se(2)—C(12)	1.918(13)	C(20)–Ru(1)–Se(1)	163.0(5)
	Se(2)—C(11)	1.985(12)	Cl(1)–Ru(1)–Se(1)	85.23(9)
			C(23)–Ru(1)–Se(2)	138.3(9)
			C(22)–Ru(1)–Se(2)	104.5(5)
			C(21)–Ru(1)–Se(2)	86.8(5)
			C(19)–Ru(1)–Se(2)	134.0(12)
			C(18)–Ru(1)–Se(2)	166.7(8)
			C(20)–Ru(1)–Se(2)	101.5(7)
			Cl(1)–Ru(1)–Se(2)	90.81(9)
			Se(1)–Ru(1)–Se(2)	91.74(5)
			C(1)–Se(1)–C(7)	98.2(5)
			C(12)–Se(2)–C(11)	101.9(6)
			C(12)–Se(2)–Ru(1)	102.4(4)
			C(11)–Se(2)–Ru(1)	109.9(3)

IR Data

L (KBr, cm^{-1}): 3012($\nu_{C—H(aromatic)}$), 2908($\nu_{C—H(aliphatic)}$), 1564($\nu_{C=C(aromatic)}$), 733($\nu_{C—H(aromatic\ bend)}$).

1 (KBr, cm^{-1}): 3032($\nu_{C—H(aromatic)}$), 2896($\nu_{CH(aliphatic)}$), 1589 ($\nu_{C=C(aromatic)}$), 1089 and 630 ($\nu_{Cl—O}$), 733($\nu_{C—H(aromatic\ bend)}$)

2 (KBr, cm^{-1}): (KBr, cm^{-1}): 3046($\nu_{C—H(aromatic)}$), 2873($\nu_{C—H(aliphatic)}$), 1604−1467($\nu_{C=C(aromatic)}$ and $\nu_{C=N(aromatic)}$), 734($\nu_{C—H(aromatic\ bend)}$).

3 (KBr, cm^{-1}): 3213($\nu_{C—H(aromatic)}$), 2842($\nu_{C—H(aliphatic)}$), 1534($\nu_{C=C(aromatic)}$), 845($\nu_{P—F(aromatic\ bend)}$), 730($\nu_{C—H(aromatic\ bend)}$).

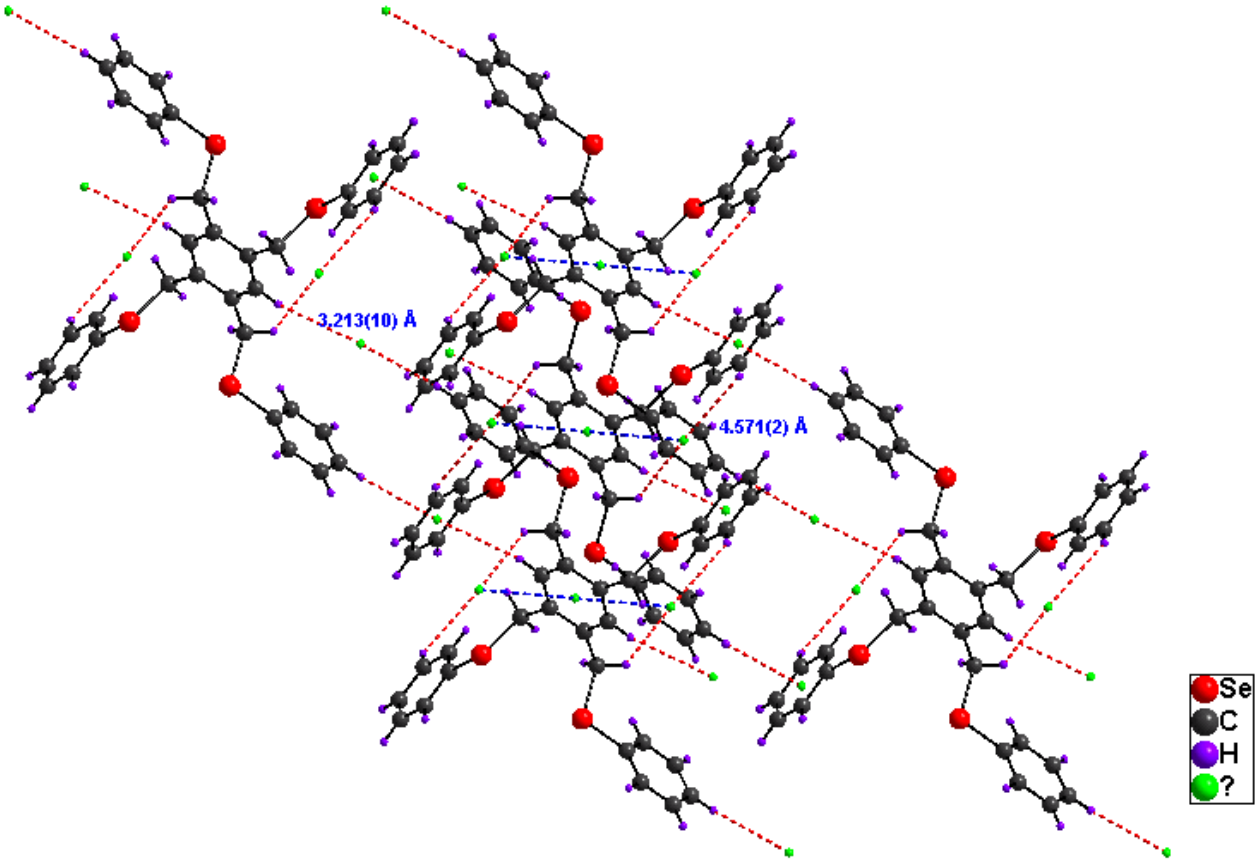

Fig S1. C–H···π and π···π interactions in **L**

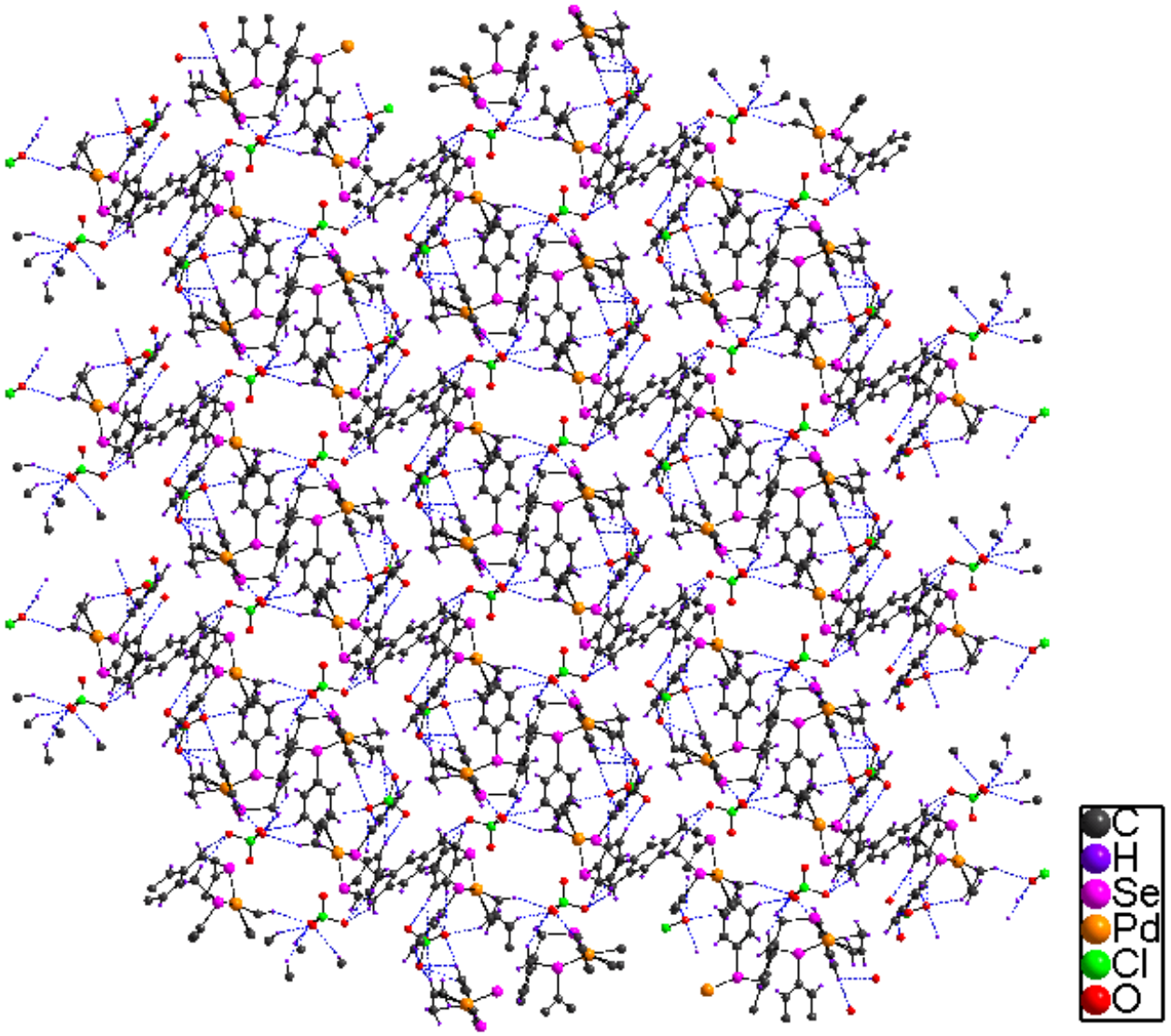

Fig S2. In **1** 3-D network formation as a result of weak O···H interactions;
2.384(15) – 2.968(18) Å

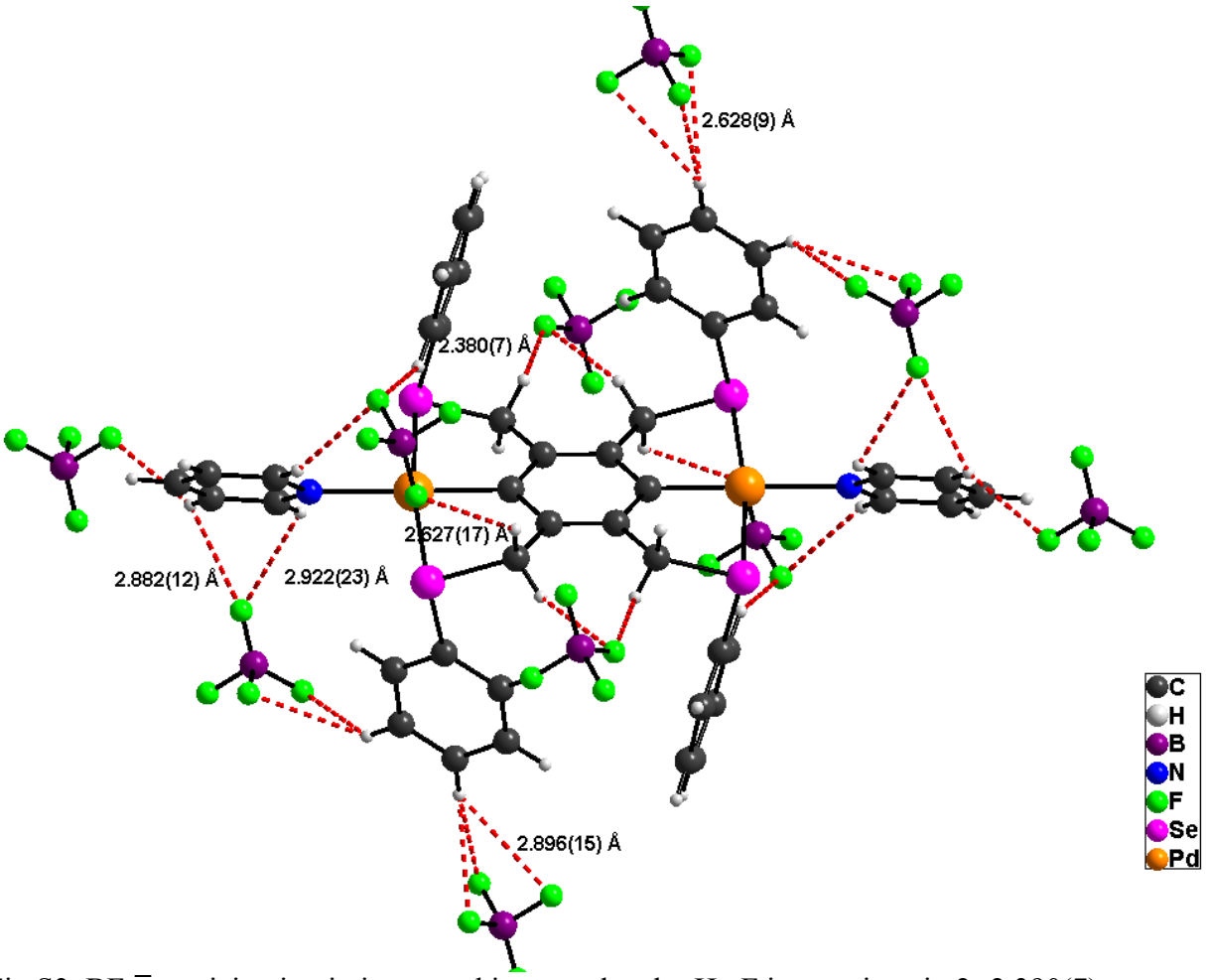

Fig S3. BF_4^- participating in intra- and inter-molecular H···F interactions in **2;** 2.390(7)-2.922(23) Å

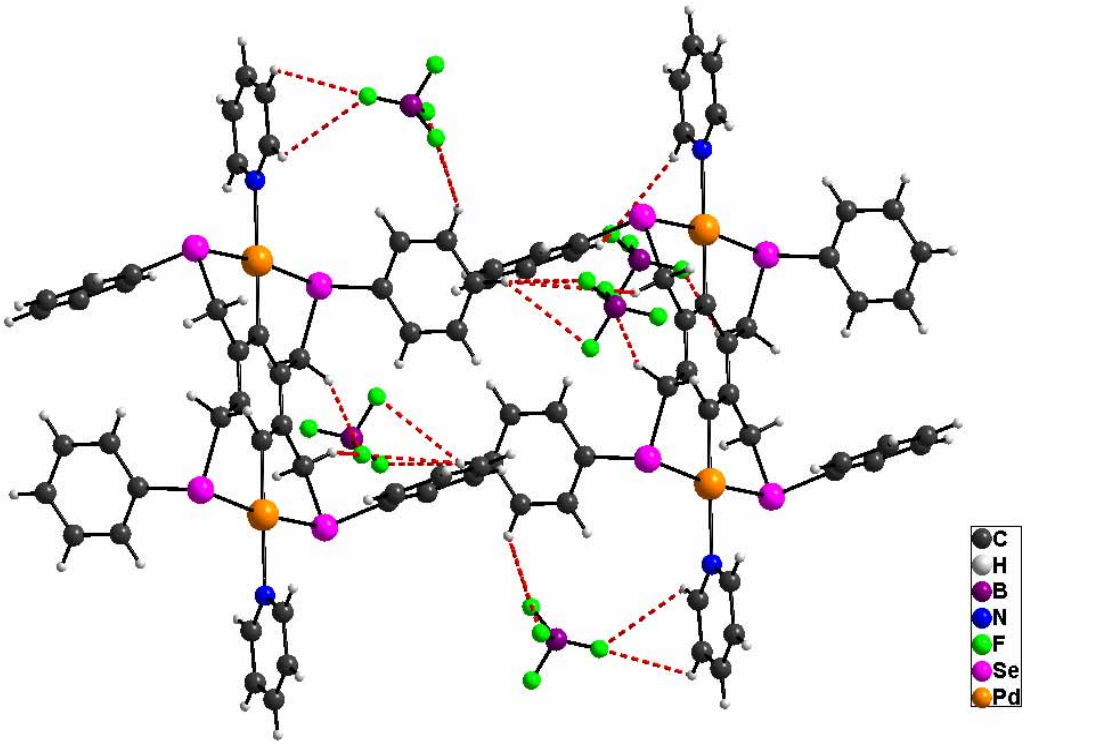

Fig S4. Two cationic units $[Pd_2(Py)_2(\mathbf{L})]^{2+}$ linked by BF_4^- through H···F interactions

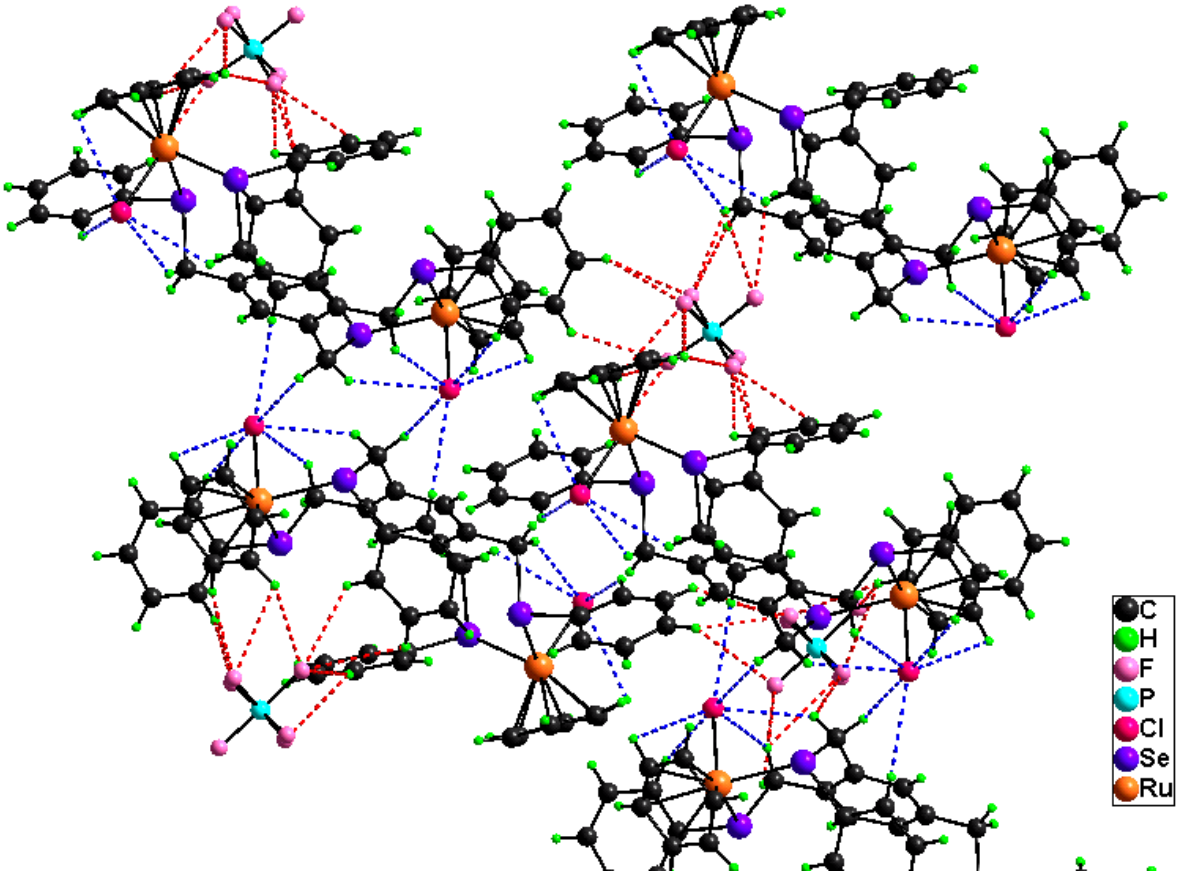

Fig S5. Complex 3-D network formation in **3** as a result of weak H···F and H···Cl interactions H···F length range 2.649(16) – 3.051(18) Å, H···Cl length range 2.703(4) – 3.025(3) Å

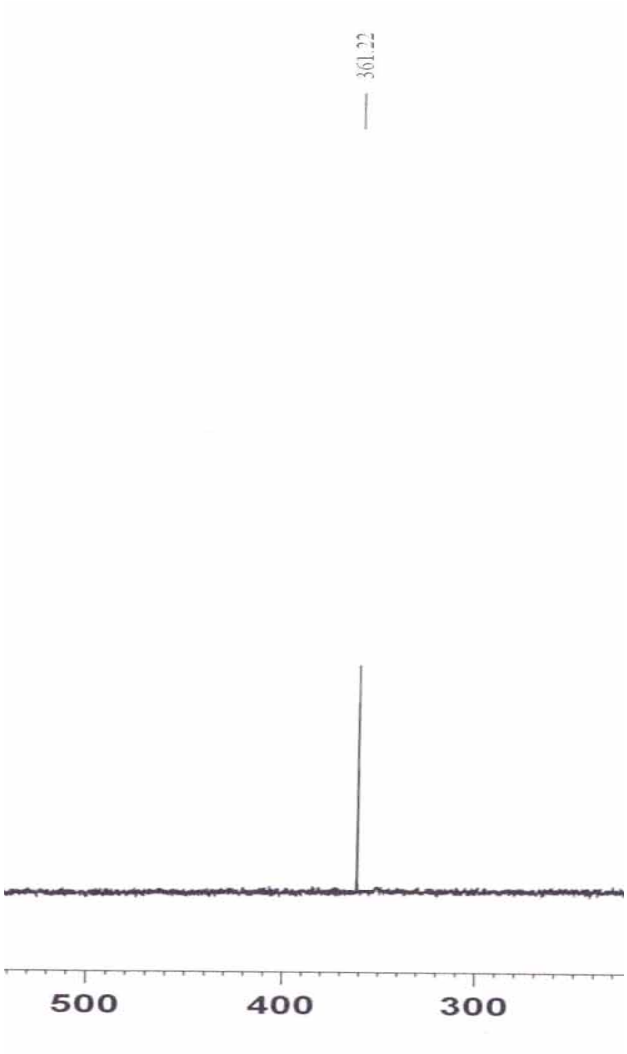

Fig S6. $^{77}Se\{^{1}H\}$ NMR of **L**

Fig S7. $^{77}Se\{^{1}H\}$ NMR of **1**

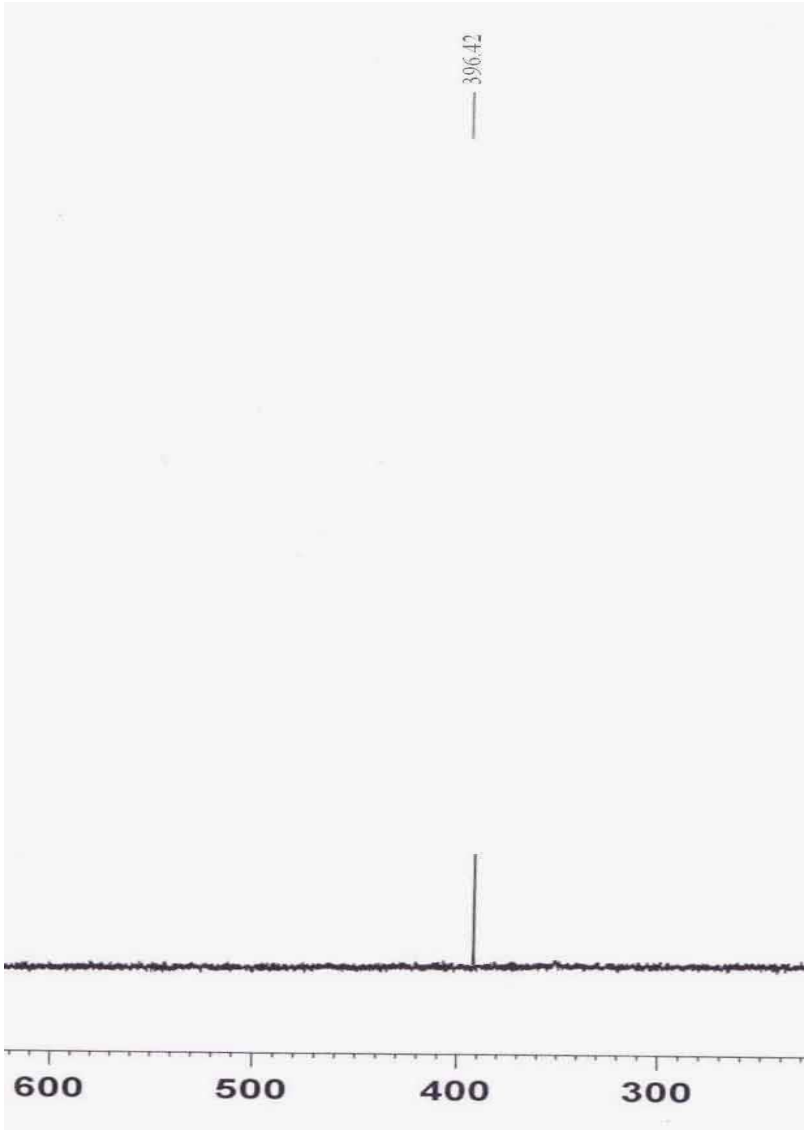

Fig S8. $^{77}Se\{^{1}H\}$ NMR of **2**

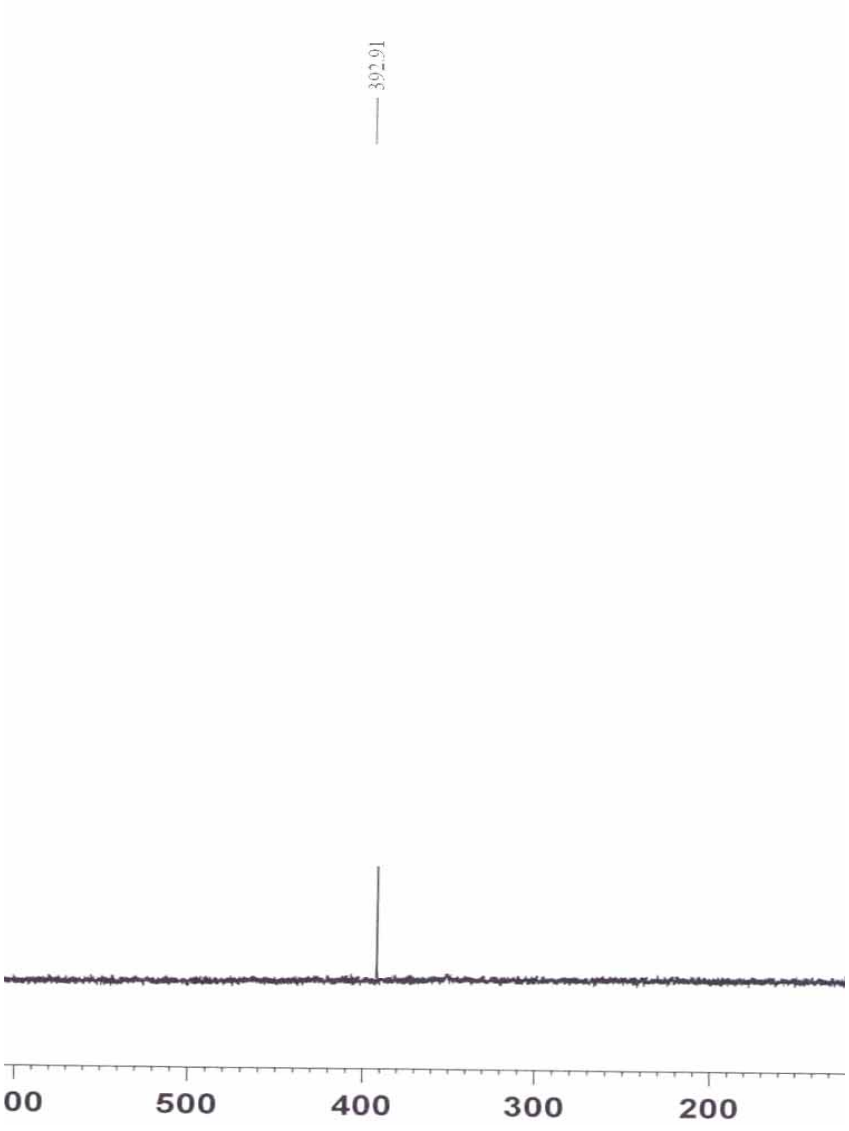

Fig S9. $^{77}Se\{^{1}H\}$ NMR of **3**