Gold and nickel alkyl substituted bis-thiophenedithiolene complexes; anionic and neutral forms

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Electronic Supplementary Information (ESI)

Crystal structure of **III**:

Compound **III** was obtained as white needles and it crystallized in the orthorhombic system, space group P 2_1 2_1 2_1. The unit cell contains one neutral molecule at general position. The bond lengths are within the expected range for thiophenic dithiol ketones (Table S1, Figure S1). The crystal structure is similar to that found for the related compound **II** (R. A. L. Silva, B.J.C. Vieira, M. M. Andrade, I. C. Santos, S. Rabaça, D. Belo, M. Almeida, *Beilstein J. Org. Chem*. **2015**, *11*, 628–637). It is composed by layers, piled along *b*, of pairs of side-by-side chains of the ketone running parallel to *a*. Within these bi-chains, arranged in a herringbone type mode, the molecules are connected by short S···O contacts, with the isopropyl groups pointing outside the bi-chains. Molecules in different chains make an angle of circa 87.6°. There are no short contacts between bi-chains in the same layer. Molecules in different layers are connected by short S···$C_{\text{double bond}}$ contacts and S···H-C bond hydrogen bonds (Table S2, Figure S2).

Table S1. Bond lengths in the crystal structure of compound **III**.

	d (Å)
S1-C1	1.782(3)
S1-C2	1.739(3)
S2-C2	1.708(3)
S2-C3	1.747(2)
S3-C1	1.779(3)
S3-C7	1.749(3)
O1-C1	1.208(3)
C2-C7	1.354(4)
C3-C4	1.509(4)
C3-C6	1.365(4)
C4-C5	1.527(4)
C4-C11	1.532(4)
C6-C7	1.435(3)
C6-C8	1.510(3)
C8-C9	1.532(4)

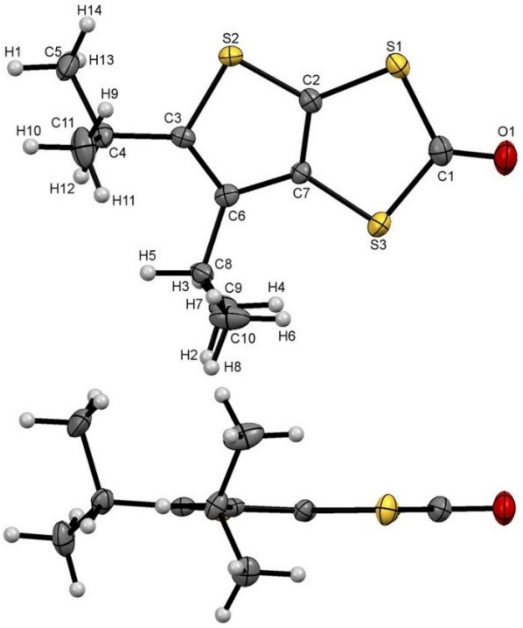


Figure S1. ORTEP and atomic numbering scheme of compound **III**, with thermal ellipsoids at 50% probability level.

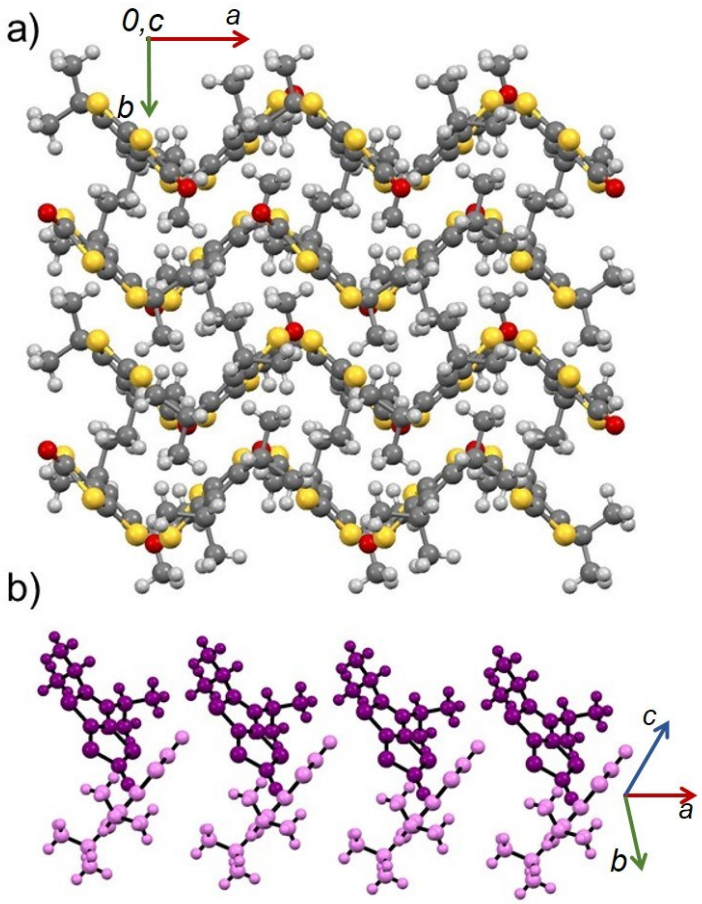


Figure S2. Crystal structure of **III** a) viewed along the *c axis; b*) detail showing the bi-chains, which constitute the layers.

Table S2. Short contacts and hydrogen bonds in the crystal structure of compound **III**.

	d (Å)	Symm. Opp.	angle (°)
S1···O1	3.155	-1/2+x,1.5-y,-z	
S1···H1-C5	3.097	1.5-x,1-y, -1/2+z	119.4
S2··· O1	3.311	-1/2+x,1.5-y,-z	
S2···H7-C10	3.061	1-x,-1/2+y,1/2-z	167.3
S3···H3-C5	3.087	2-x,1/2+y,1/2-z	140.9
S3···H13-C5	3.099	2-x,1/2+y,1/2-z	139.2
S3···C3=C6$_{(double\ bond)}$	3.433	2-x,1/2+y,1/2-z	
C2=C7$_{(double\ bond)}$···H1-C5	2.899	1-x,-1/2+y,1/2-z	119.5

Table S3. Bond lengths in the crystal structure of compound **1**.

	d (Å)
Au1-S1	2.3113
Au1-S2	2.315
S1-C2	1.754(4)
S2-C1	1.748(3)
C1-C2	1.347(5)
C1-S3	1.764(4)
C2-C3	1.420(7)
C4-C5	1.507(4)
C4-S3	1.749(3)
C4-C3	1.356(8)
C5-C6	1.544(5)
C5-C7	1.532(5)
C5-C8	1.528(5)

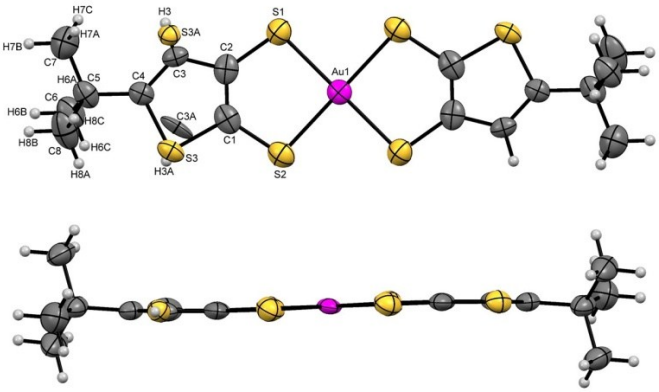


Figure S3. ORTEP and atomic numbering scheme of compound **1**, with thermal ellipsoids at 50% probability level.

Table S4. Short contacts and hydrogen bonds in the crystal structure of compound **1.**

	d (Å)	Symm. Opp.	angle (°)	Interaction
S3···S3	3.413	1/2-x,1/2-y,-z		Anionic Chain
C6-H6C···S2	3.036	1/2-x,1/2-y,-z	139.8	Anionic Chain
C22-H22···S1	2.963	x,y,z	154.5	Anionic Cation
C21-H21···S2	3.054	x,y,z	126.7	Anionic Cation

Table S5. Bond lengths in the crystal structure of Compound **2**.

	d (Å)
Ni1-S1	2.1566
Ni1-S2	2.1613
S1-C2	1.735(2)
S2-C1	1.723(2)
C1-C2	1.362(3)
C1-S3	1.752(3)
C2-C3	1.419(5)
C4-C5	1.512(3)
C4-S3	1.745(2)
C4-C3	1.358(7)
C5-C6	1.526(4)
C5-C7	1.539(3)
C5-C8	1.533(4)

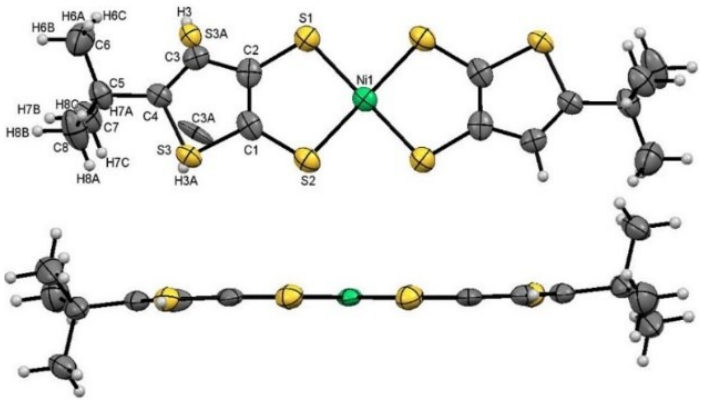


Figure S4. ORTEP and atomic numbering scheme of compound **2**, with thermal ellipsoids at 50% probability level.

Table S6. Short contacts and hydrogen bonds in the crystal structure of Compound **2**.

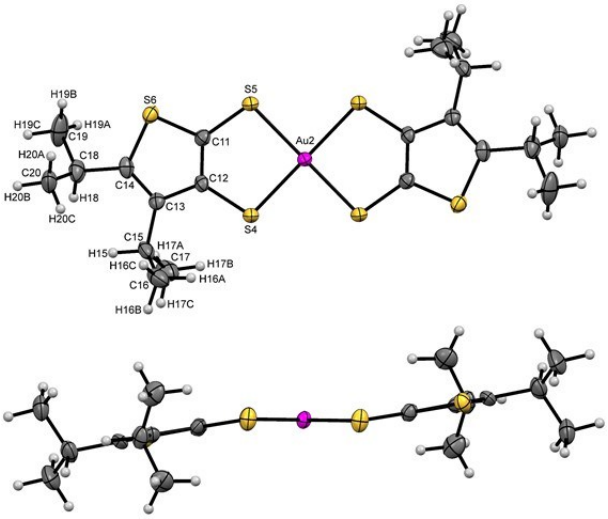
	d (Å)	Symm. Opp.	angle (°)	Interaction
S3-S3	3.446	1/2-x,1/2-y,-z		Anionic Chain
S1···H22-C22	2.954	x,y,z	152.2	Anion-Cation
S2···H21-C21	3.078	x,y,z	124.3	Anion-Cation

Table S7. Bond lengths in the crystal structure of compound **3**, molecule A.

	d (Å)
Au1-S1	2.301
Au1-S2	2.305
S1-C1	1.740(5)
S2-C2	1.768(5)
S3-C1	1.728(5)
S3-C4	1.726(6)
C1-C2	1.345(7)
C2-C3	1.431(7)
C3-C4	1.344(9)
C3-C5	1.506(7)
C4-C8	1.521(9)
C5-C6	1.53(1)
C5-C7	1.523(9)
C8-C9	1.55(1)
C8-C10	1.51(1)

Table S8. Bond lengths in the crystal structure of compound **3**, molecule B.

	d (Å)
Au2-S4	2.313
Au2-S5	2.305
S4-C12	1.759(5)
S5-C11	1.761(5)
S6-C11	1.712(5)
S6-C14	1.742(6)
C11-C12	1.360(7)
C12-C13	1.450(7)
C13-C14	1.360(7)
C13-C15	1.500(8)
C14-C18	1.498(8)
C15-C16	1.532(7)
C15-C17	1.539(8)
C18-C19	1.515(9)
C18-C20	1.523(8)



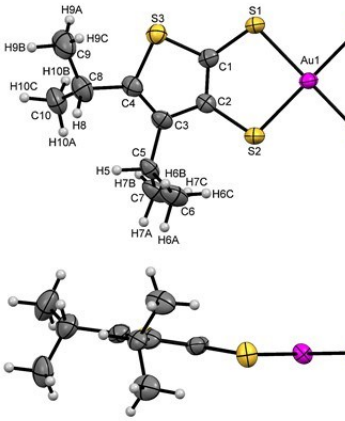


Figure S5. ORTEP and atomic numbering scheme of complexes in compound **3**, with thermal ellipsoids at 50% probability level.

Table S9. Short contacts and hydrogen bonds in the crystal structure of compound **3.**

	d (Å)	Symm. Opp.	angle (°)	Interaction
S3···S5	3.677	-x,1-y,1-z	-	Anion-Anion
S3···S6	3.681	-x,1-y,1-z		Anion-Anion
C45···H45···S2	2.875	1-x,-y,1-z	164.4	Cation-Anion

C25-H25···S2	2.956	x,y,z	142.8	Cation-Anion
S3···H55-C55	3.096	x,y,z	115.7	Cation-Anion
S4···H33-C33	3.011	-1+x,y,-1+z	148.4	Cation-Anion
S6···H23-C23	3.014	-1+x,y,-1+z	138.3	Cation-Anion
S6···H44-C44	3.042	x,1+y,-1+z	139.6	Cation-Anion
C54-H54···S4	2.874	x,y,1+z	152.3	Cation-Anion
C33-H33···C11$_{\text{double bond}}$	2.765	1+x,y,1+z	150.1	Cation-Anion
C33-H33···C12 $_{\text{double bond}}$	2.690	1+x,y,1+z	176	Cation-Anion

Table S10. Bond lengths in the crystal structure of compound **4**, molecule A.

	d (Å)
Ni1-S1	2.1548
Ni1-S2	2.1630
S1-C1	1.722(2)
S3-C1	1.724(2)
S3-C4	1.747(2)
S2-C2	1.739(2)
C1-C2	1.373(3)
C4-C8	1.516(3)
C4-C3	1.362(3)
C8-C9	1.540(3)
C8-C10	1.529(3)
C3-C5	1.515(3)
C3-C2	1.444(3)
C5-C7	1.530(3)
C5-C6	1.520(3)

Table S11. Bond lengths in the crystal structure of Compound **4**, molecule B.

	d (Å)
Ni2-S4	2.1588
Ni2-S5	2.1584
S4-C12	1.741(2)
S5-C11	1.719(2)
S6-C11	1.730(2)
S6-C14	1.747(2)
C12-C11	1.375(3)
C12-C13	1.442(3)
C14-C18	1.516(3)
C14-C13	1.366(3)
C18-C19	1.518(4)
C18-C20	1.529(3)
C13-C15	1.508(3)
C15-C17	1.534(3)
C15-C16	1.521(3)

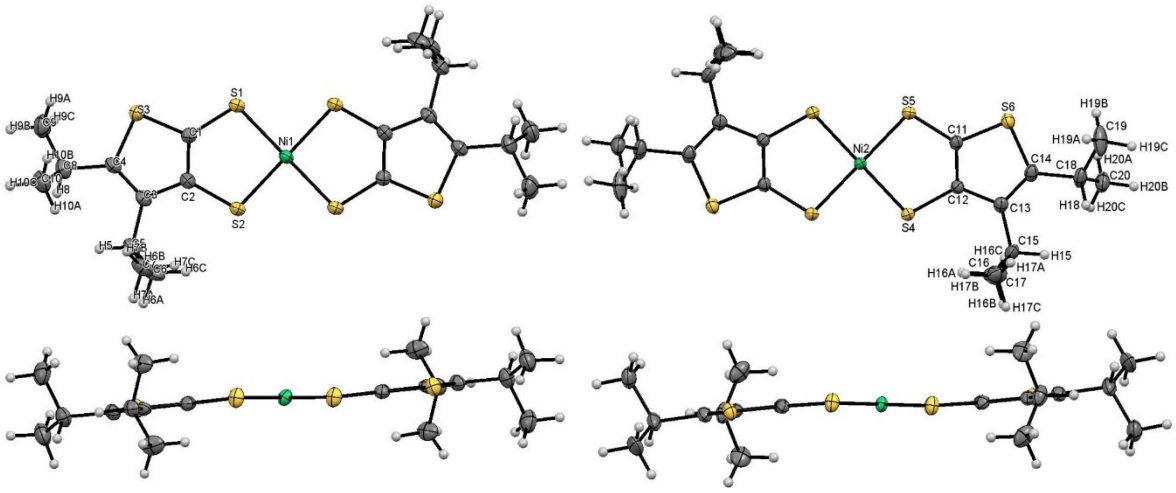


Figure S6. ORTEP and atomic numbering scheme of complexes in compound **4**, with thermal ellipsoids at 50% probability level.

Table S12. Short contacts and hydrogen bonds in the crystal structure of compound **4.**

	d (Å)	Symm. Opp.	angle (°)	Interaction
S3···S6	3.642	-x,1-y,1-z	-	Anion-Anion
S2···H25-C25	2.892	x,y,z	142.9	Anion-Cation
S2···H45-C45	2.936	x,1+y,z	161.3	Anion-Cation
S4-H33-C33	2.931	-1+x,y,-1+z	149.7	Anion-Cation
S4···H54-C54	2.905	x,y,-1+z	151.5	Anion-Cation
S6···H23-C23	2.989	-1+x,y,-1+z	140.79	Anion-Cation
C11=C12···H33	2.782	-1+x,y,-1+z	173.2	Anion-Cation
C11=C12···H23	2.772	-1+x,y,-1+z	126.2	Anion-Cation

Table S13. Bond lengths in the crystal structure of compound **5**.

	d (Å)
Au1-S1	2.320(1)
Au1-S2	2.321(1)
Au1-S3	2.294(1)
Au1-S4	2.299(1)
S1-C1	1.714(6)
S2-C2	1.690(5)
S3-C9	1.745(6)
S4-C10	1.739(6)
S5-C2	1.751(6)
S5-C4	1.710(6)
C3-C1	1.39(2)
C3-C4	1.40(1)
S6-C10	1.749(7)
S6-C12	1.691(7)
C11-C9	1.46(2)
C11-C12	1.36(2)
C1-C2	1.397(7)
C4-C5	1.507(8)
C5-C6	1.53(1)
C5-C7	1.530(9)
C5-C8	1.537(8)
C9-C10	1.349(7)
C12-C13	1.520(9)
C13-C14	1.63(1)
C13-C15	1.55(1)
C13-C16	1.43(1)

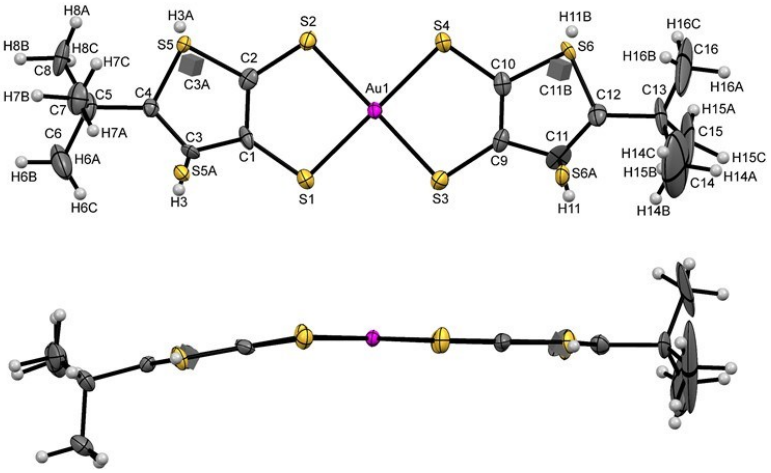


Figure S7. ORTEP and atomic numbering scheme of compound **5**, with thermal ellipsoids at 50% probability level.

Table S14. Short contacts and hydrogen bonds in the crystal structure of compound **5.**

	d (Å)	Symm. Opp.	angle (°)	Interaction
S2···S1	3.499	1+x,y,z	-	dimer
S4···S1	3.552	-1+x,y,z	-	intrachains
S4···S3	3.534	-1+x,y,z	-	intrachains
S2···S2	3.517	-x,2-y,-z	-	intrachains
S2···S4	3.419	-x,2-y,-z	-	intrachains
S6···H6A-C6	2.921	1-x,2-y,-z	173.7	dimer
C11···H8c-C8	2.855	1-x,2-y,-z -	170.3	dimer
S6···H7b-C7	2.981	-1/2+x,1.5-y,1/2+z	143.6	interchains

Table S15. Bond lengths in the crystal structure of compound **6**.

	d (Å)
Ni1-S1	2.144(1)
Ni1-S2	2.144(1)
Ni1-S4	2.146(1)
Ni1-S5	2.145(1)
S1-C1	1.694(4)
S2-C2	1.689(3)
S4-C9	1.706(4)
S5-C10	1.699(4)
S6-C10	1.765(4)
S6-C12	1.768(4)
C11-C9	1.42(1)
C11-C12	1.35(1)
C1-C2	1.398(5)
C1-S3	1.731(5)
C2-C3	1.43(1)
C4-C5	1.518(4)
C4-S3	1.730(5)
C4-C3	1.36(1)
C5-C6	1.544(4)
C5-C7	1.528(5)
C5-C8	1.521(5)
C9-C10	1.377(5)
C12-C13	1.506(5)
C13-C14	1.514(5)
C13-C15	1.518(6)
C13-C16	1.515(7)

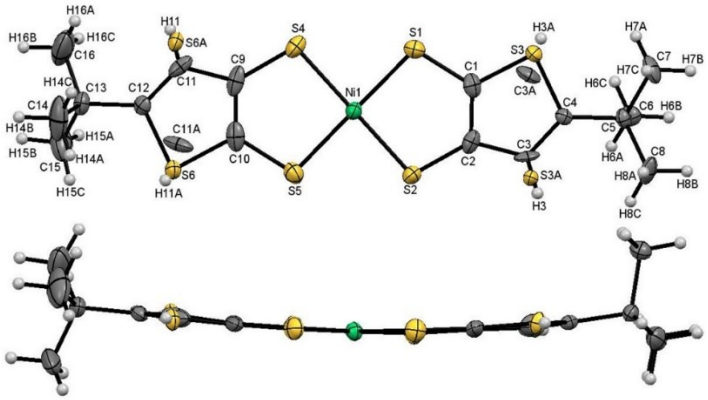


Figure S8. ORTEP and atomic numbering scheme of compound **6**, with thermal ellipsoids at 50% probability level.

Table S16. Short contacts and hydrogen bonds in the crystal structure of compound **6.**

	d (Å)	Symm. Opp.	angle (°)	Interaction
S3···S3	3.443	1-x,-y,-z		within the layer
S2···S2	3.682	-x,-y,1-z		within the layer
S6···H7C-C7	2.937	-x,-y,1-z	164.5	within the dimer
C10=C9···H14B	2.764	-1/2+x,1/2-y,-1/2+z	163.9	between layers

Table S17. Bond lengths in the crystal structure of Compound **7**.

	d (Å)
Au1-S1	2.309
Au1-S2	2.296
S1-C2	1.730(5)
S2-C1	1.715(5)
S3-C1	1.719(5)
S3-C4	1.746(5)
C1-C2	1.394(7)
C2-C3	1.442(6)
C3-C4	1.363(7)
C3-C5	1.515(7)
C4-C6	1.519(6)
C5-C7	1.521(8)
C5-C8	1.535(7)
C5-H5	0.90(4)
C6-C9	1.518(8)
C6-C10	1.523(8)

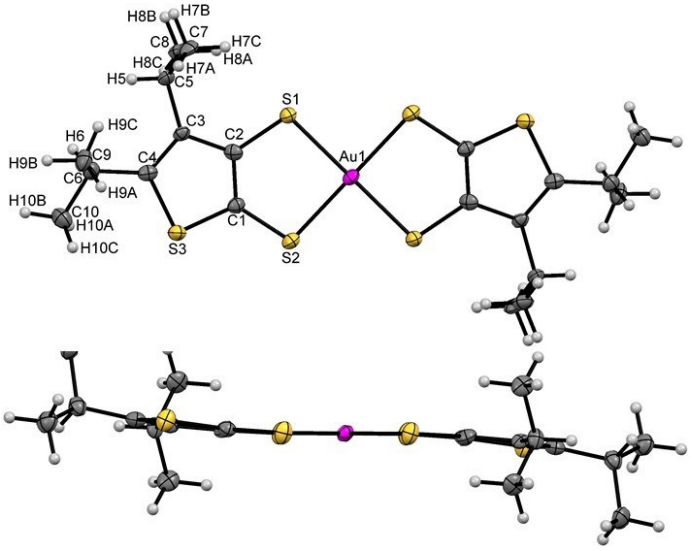


Figure S9. ORTEP and atomic numbering scheme of compound **7**, with thermal ellipsoids at 50% probability level.

Table S18. Short contacts and hydrogen bonds in the crystal structure of compound **7.**

	d (Å)	Symm. Opp.	angle (°)	Interaction
C1=C2···H10A	2.803	-1+x,y,z	168.2	column

Table S19. Bond lengths in the crystal structure of compound **8**.

	d (Å)
Ni1-S1	2.1468
Ni1-S2	2.1382
S1-C2	1.712(2)
S2-C1	1.695(2)
S3-C1	1.723(2)
S3-C4	1.746(2)
C1-C2	1.396(3)
C2-C3	1.447(3)
C3-C4	1.364(3)
C3-C5	1.509(3)
C4-C6	1.516(3)
C5-H5	1.000
C5-C7	1.536(3)
C5-C8	1.533(4)
C6-H6	1.000
C6-C10	1.525(3)
C6-C9	1.518(4)
C7-H7A	0.980
C7-H7C	0.979
C7-H7B	0.980
C10-H10B	0.980
C10-H10A	0.980
C10-H10C	0.980
C8-H8B	0.980
C8-H8A	0.980
C8-H8C	0.980
C9-H9B	0.981
C9-H9C	0.980
C9-H9A	0.980

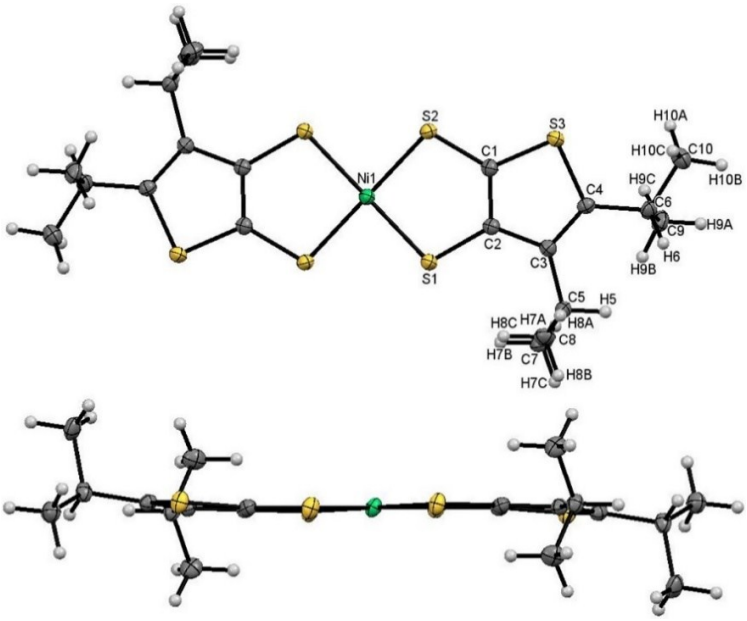


Figure S10: ORTEP and atomic numbering scheme of compound **8**, with thermal ellipsoids at 50% probability level.

Table S20. Short contacts and hydrogen bonds in the crystal structure of compound **8.**

	d (Å)	Symm. Opp.	angle (°)	Interaction
C1=C2···H10c	2.805	-1+x,y,z	172	column

UV-Vis Spectroscopy of the Ni and Au complexes (**1**-**8**):

In the nickel complexes **6** and **8**, it is observed a strong absorption band at the lower energy region, at ~850 nm, typical of neutral nickel complexes. This intense band is usually attributed to the π-π* transition between the frontier orbitals: the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). In the case of the corresponding monoanionic complexes, **2** and **4**, this band should appear shifted to lower energies, above the upper limit of the spectra, with decrease intensity. In the electronic absorption spectra of **2** and **4**, a slight increase of the slope in the upper limit of the spectra is observed, indicative of the formation of this band.

The spectra of complexes **1** and **3**, display rather high energy absorption bands, in the UV region, below 260 nm. These bands are ascribed to the d-d transitions and are typical of monoanionic gold complexes (P. Basu, A. Nigam, B. Mogesa, S. Denti, V.N. Nemykin, *Inorg. Chim. Acta* **2010**, *363*, 2857).

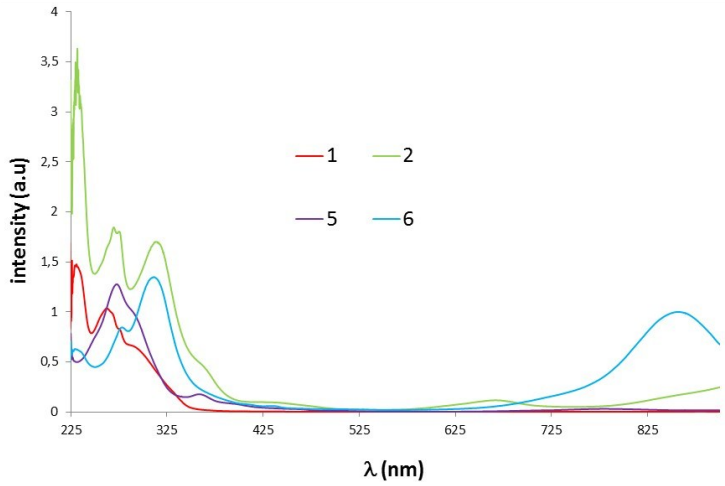


Figure S11: UV-Vis Spectra of compounds **1**, **2**, **5** and **6**.

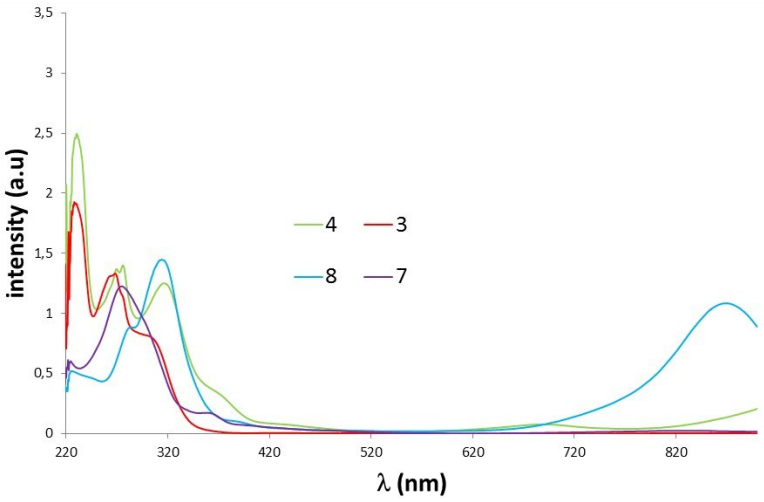


Figure S12: UV-Vis Spectra of compounds **3**, **4**, **7** and **8**.

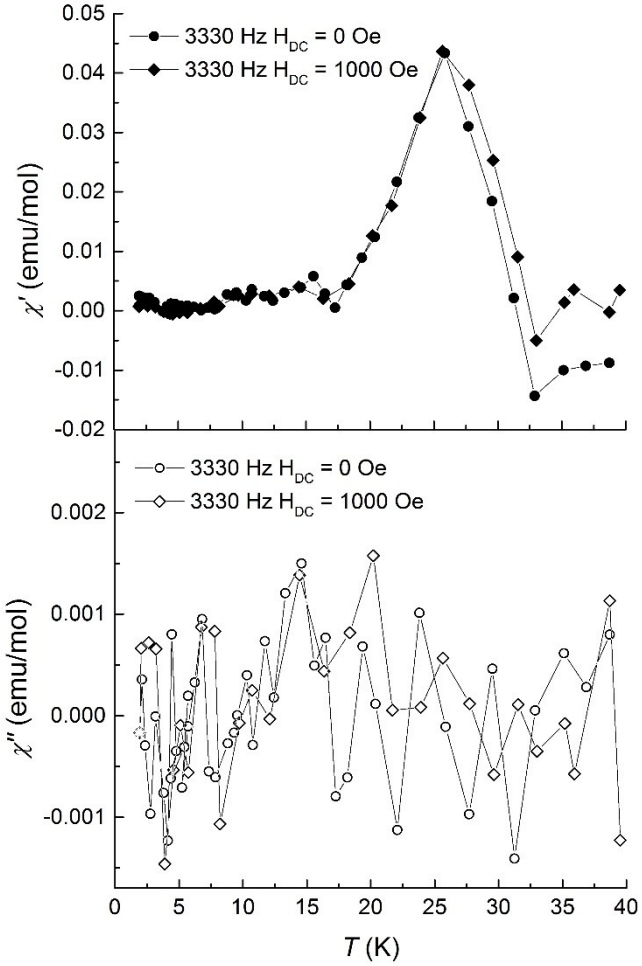


Figure S13: Temperature dependence of the real and imaginary components of AC susceptibility, χ' and χ'', of **7** at 3330 Hz under static magnetic fields of 0 and 1000 Oe.