Electronic Supplementary Information for Dalton Transactions

==========

SUPPLEMENTARY MATERIAL

==========

BELONGING TO THE PAPER

Gold(I) Derived Thiosemicarbazone Complexes with rare halogen-halogen interaction – Reduction of [Au(damp-C^1,N)Cl_2]

by

Setshaba D. Khanye,[a] Nikoletta B. Báthori,[a] Gregory Smith,[a] and Kelly Chibale*[a,b]

[a] Department of Chemistry, University of Cape Town, Rondebosch 7701, South Africa

[b] Institute of Infectious Disease and Molecular Medicine, University of Cape Town, Rondebosch 7701, South Africa,

Phone: +27-21-650-2553, Fax: +27-21-689-7499, E-mail: Kelly.Chibale@uct.ac.za

1. Single Crystal X-ray Diffraction

Summary of X-ray crystallography. Crystal intensity data were collected on a Nonius Kappa CCD Single Crystal X-ray Diffractometer, using a graphite monochromated MoKα radiation (λ= 0.7107 Å, T= 173K) generated by a Nonius FR590 generator at 50 kV and 30 mV. A series of frames were recorded, each of width 1º in ϕ or in ω to ensure completeness of the data collected to θ>28º. The unit cell was indexed from the first 10 frames, and positional data were refined along with diffractometer constants to give the final cell parameters. The strategy for data collection was evaluated using COLLECT[1] software. Integration and scaling (DENZO and Scalepack[2]) resulted in unique data sets corrected for Lorentz polarization effects and for the effects of crystal decay and absorption by a combination of averaging of equivalent reflection and overall volume and scaling correction. Accurate unit cell parameters were refined on all data. The structures were solved using SHELXS-97[3] and refined using full-matrix least squares methods in SHELXL-97[3], with the aid of the program X-Seed.[4] The analysis of short contacts was carried out using PLATON.[5]

Crystal data for 1 (CCDC No.720892)**:** a) The crystals of **1** were grown by slow evaporation from a solution of acetonitrile. $C_{18}H_{20}N_6Au_1Br_2S_2^+.Cl^-.2(C_2H_3N)$, M = 858.86, Monoclinic, C2/c (No. 15), a= 11.846(2)Å, b= 10.358(2)Å, c= 24.577(5)Å, β= 101.89(3)°, V= 2950.9(10)Å3, Z=4, Dcalc= 1.933 Mg/m3, μ= 7.952mm-1, F(000)= 1648, crystal size: 0.01x 0.01x 0.01mm, T=173K, MoKα=0.71073Å, Θmin-max= 2.6-25.3°, No. of total reflections= 12752, No. of uniq reflections= 2705, Rint= 0.055, No. of I>2.0sigma(I)= 2313, Nref= 2705, Npar= 167, R= 0.0321, wR2= 0.0688, S= 1.05, w=1/[s2\(Fo2)+(0.0517P)2+0.1749P] where P=(Fo2+2Fc2)/3), Max. and Av. Shift/Error= 0.00, 0.00, Min. and Max. Resd. Dens.=-0.83, 1.12e/Å3.

Crystal data for 2 (CCDC No. 720893)**:** b) The crystals of **2** were grown by slow evaporation from a solution of acetonitrile. $C_{18}H_{18}N_6S_2AuCl_4^+.Cl^-.2(C_2H_3N)$, M = 838.83, Monoclinic, C2/c (No. 15), a= 11.776(2)Å, b= 10.658(2)Å, c= 24.515(5)Å, β= 96.79(3)°, V= 3055.3(10)Å3, Z=4, Dcalc= 1.824Mg/m3, μ= 5.417 mm-1, F(000)= 1632 crystal size: 0.05x 0.05x 0.05mm, T=173K, MoKα=0.71073Å, Θmin-max= 2.6-25.7°, No. of total reflections= 9300, No. of uniq reflections= 2889, Rint= 0.040, No. of I>2.0sigma(I)= 2377, Nref= 2889, Npar= 176, R= 0.0330, wR2= 0.0702, S= 1.07, w=1/[s2\(Fo2)+(0.0517P)2+0.1749P] where P=(Fo2+2Fc2)/3), Max. and Av. Shift/Error= 0.00, 0.00, Min. and Max. Resd. Dens.= -1.18, 1.74e/Å3.

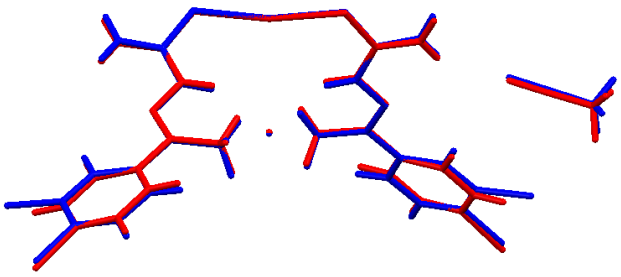

Figure S1: RMS of overlay fit of the two molecules is 0.0279Å (all atoms were overlayed from **1** and **2** from the gold-coordinated thiosemicarbazone cation except the aromatic halogens.[6]

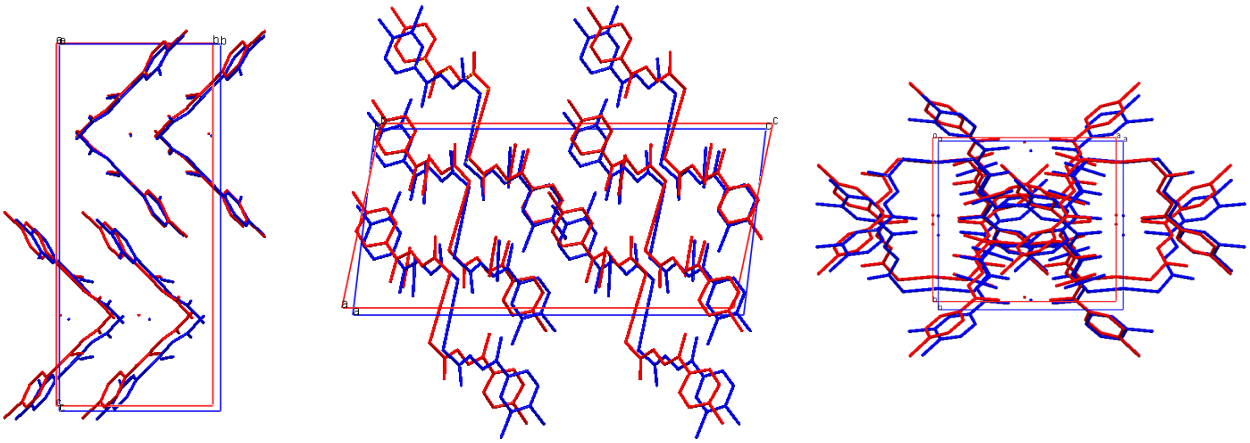

Figure S2: The fitted structure of 1 (red) and 2 (blue) from view down a axis (a), b axis (b) and c axis (c).

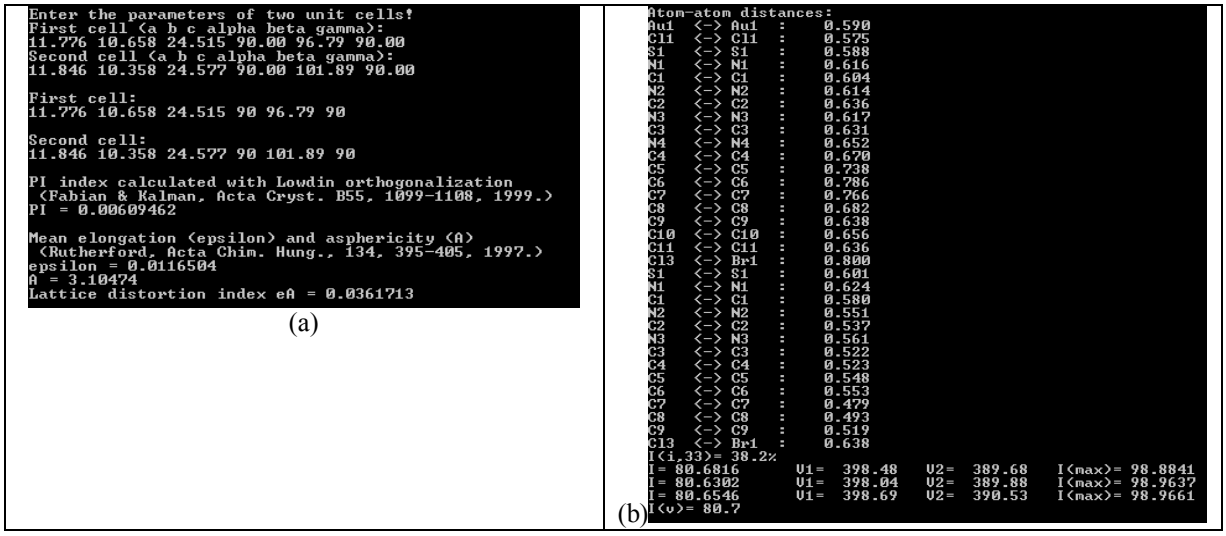

Figure S3: Results of cell similarity (a) and isostructurality (b) calculation of **1** and **2**. The following indices were used to comparison of structures: (i) cell similarity index: $\Pi=[(a+b+c)/(a'+b'+c')]-1$, where *a, b, c* and *a', b' c'* are the orthogonalized lattice parameters of the related crystals. In the event of great similarity of the two unit cells π is lose to zero. (ii) mean elongation: $\varepsilon=(V'/V)^{1/3}-1$, which describes the difference in cell size, while (iii) asphericity index: $A=(2/3)[1-\sum_{j>i}\{[(1+\varepsilon)M_i-1]x[(1+\varepsilon)M_j-1]/3\varepsilon^2\}^{1/2}$ accounts for the shape distortion. In the event of great similarity of the

two unit cells ε and A close to zero. (iv) isostructurality index: $I_i(n)=[1-(\sum R^2_i/n)^{1/2}x100\%$. $I_i(n)$ takes into account both the differences in the geometry of the molecules and the positional differences caused by rotation and translation. The isostructurality index for **1** and **2** was calculated for 33 heavy atoms. (v) volumetric isostructurality index: $I_v= 2V_0/(V_1+V_2)$x100%, expressed as the ratio of volume overlap to the average volume. In the event of great similarity of the two unit cells I_v close to 100%, when (vi) $I_{vmax}= (2\min\{V_1, V_2\})/(V_1+V_2)$x100% when $V_1 \neq V_2$ is the theoretical maximum of *T*he cell similarity index, $\prod = 0.006$, the lattice distortion index, $\varepsilon A = 0.035$. The isostructurality indices show the two structures are isostructural ($I_v = 80.7\%$, $I_{vmax}=98.9\%$).

Analysis of Cl...Cl contact in structure 2: The Cambridge Structural Database (version 5.29, November 2008) was searched for Cl...Cl intermolecular contacts within the sum of their van der Waals radii with the following filters:R factor < 0.05, no errors in crystal structures, no ions, not disorder, not polymeric, no powder structures, 3D coordinates determined. No any refcode restriction was applied. We got 39 hits and they were refined with the following filters: (i) -C(X)-C(X)- torsion angle= *ca*.-5 - +5, (ii) the angle of the fitted plane for -C(X)-C(X)- atoms and for the corresponding atom pairs (-C(X')-C(X')-) is close to 0 and (iii) the distance of the previously defined planes is < 1Å. All the chlorine tetramers are built from symmetry generated chlorine-chlorine dimers and the halogens atom is bonded to an sp^2 carbon, promoting the planarity of the interaction. The final number of analyzed hits is 16 and they are detailed in Table 1.

Table S1: Summary of the results of CSD search for Cl...Cl interaction.

	Refcode	ANG1 (°)	DIST1(Å)	TOR1 (°)
1	ATUYIX	0	3.423	-0.689
2	CABTII	0	3.454	5.473
3	COFPAO10	0	3.456	-1.826
4	DESKER01	0.034	3.499	-2.076
5	QOXWAB	0.02	3.496	1.603
6	TCLOBQ02	0	3.431	1.964
7	UFEROM	0.028	3.448	-0.84
8	WATHIJ	0.02	3.399	2.936
9	WATHOP	0	3.363	1.013
10	YEBHIW	0	3.446	2.296
11	YICPOQ	0.02	3.323	-0.478
12	ZAJFAR	0.028	3.41	-2.622
13a	EDEGIE	0	3.418	-0.192
13b	EDEGIE	0.028	3.449	2.239
14	SICLAS	0.034	3.413	0
15	NIPYER	0	3.409	1.198
16	TINWOD	0	3.453	-0.789

Table S2: Crystal Data and Details of the Structure Determination of **1**.

Crystal Data

Formula	C18 H20 N6 AU1 BR2 S2+. 2(C2 H3 N).CL-

Formula Weight		858.86	
Crystal System		Monoclinic	
Space group		C2/c	(No. 15)
a, b, c [Angstrom]	11.846(2)	10.358(2)	24.577(5)
alpha, beta, gamma [deg]	90	101.89(3)	90
V [Ang**3]		2950.9(10)	
Z		4	
D(calc) [g/cm**3]		1.933	
Mu(MoKa) [/mm]		7.952	
F(000)		1648	
Crystal Size [mm]		0.01 x 0.01 x 0.01	

Data Collection

Temperature (K)		173	
Radiation [Angstrom]		MoKa	0.71073
Theta Min-Max [Deg]		2.6, 25.3	
Dataset		-14: 14 ; -12: 12 ; -29: 29	
Tot., Uniq. Data, R(int)		12752, 2705, 0.055	
Observed data [I > 2.0 sigma(I)]	2313		

Refinement

Nref, Npar	2705, 167
R, wR2, S	0.0321, 0.0688, 1.05
w = 1/[\s^2^(Fo^2^)+(0.0282P)^2^+4.8300P] where P=(Fo^2^+2Fc^2^)/3	
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. Resd. Dens. [e/Ang^3]	-0.83, 1.12

Table S3: Final Coordinates and Equivalent Isotropic Displacement Parameters of the non-Hydrogen atoms of **1.**

Atom	x	y	z	U(eq) [Ang^2]
Au1	0	0.15149(3)	1/4	0.0311(1)
Br1	0.62417(6)	0.83019(6)	0.53292(3)	0.0638(3)
S1	0.18825(10)	0.13275(12)	0.24263(5)	0.0350(4)
N1	0.3852(3)	0.2180(4)	0.29962(17)	0.0361(12)
N2	0.2275(3)	0.3251(3)	0.31759(16)	0.0308(12)
N3	0.3062(3)	0.4030(4)	0.35342(16)	0.0318(12)
C1	0.2724(4)	0.2339(4)	0.28972(18)	0.0283(17)
C2	0.2660(4)	0.4790(4)	0.38628(19)	0.0308(16)
C3	0.1421(4)	0.4903(5)	0.3903(2)	0.0445(19)
C4	0.3530(4)	0.5612(5)	0.42226(19)	0.0343(17)
C5	0.4579(4)	0.5882(5)	0.4071(2)	0.0398(17)
C6	0.5394(5)	0.6666(5)	0.4400(2)	0.0456(17)
C7	0.5159(5)	0.7178(5)	0.4882(2)	0.0445(17)
C8	0.4160(6)	0.6906(6)	0.5046(2)	0.057(2)
C9	0.3339(6)	0.6124(6)	0.4717(2)	0.052(2)
N4	0.6153(5)	0.3334(5)	0.3549(2)	0.0582(19)
C10	0.7068(5)	0.3653(5)	0.3563(2)	0.0385(17)
C11	0.8250(4)	0.4039(6)	0.3591(2)	0.0460(17)
Cl1	0	0.47264(15)	1/4	0.0303(5)

U(eq) = 1/3 of the trace of the orthogonalized U Tensor

Table S4 - Hydrogen Atom Positions and Isotropic Displacement Parameters of 1.

Atom	x	y	z	U(iso) [Ang^2]
H1A	0.43000	0.26700	0.32430	0.0430
H1B	0.41570	0.15840	0.28160	0.0430
H2	0.15250	0.33550	0.31360	0.0370
H3A	0.11180	0.57410	0.37540	0.0670
H3B	0.13570	0.48340	0.42930	0.0670
H3C	0.09760	0.42090	0.36870	0.0670
H5	0.47360	0.55240	0.37390	0.0470
H6	0.61050	0.68480	0.42950	0.0550
H8	0.40210	0.72500	0.53840	0.0680
H9	0.26390	0.59370	0.48320	0.0620
H11A	0.87380	0.36760	0.39270	0.0690
H11B	0.83030	0.49830	0.36040	0.0690
H11C	0.85100	0.37190	0.32630	0.0690

The Temperature Factor has the Form of Exp(-T) Where
T = 8*(Pi**2)*U*(Sin(Theta)/Lambda)**2 for Isotropic Atoms

Table S5: (An)isotropic Displacement Parameters of **1.**

Atom	U(1,1) or U	U(2,2)	U(3,3)	U(2,3)	U(1,3)	U(1,2)
Au1	0.0291(2)	0.0258(2)	0.0359(2)	0	0.0010(1)	0
Br1	0.0785(5)	0.0509(4)	0.0488(4)	-0.0112(3)	-0.0173(3)	-0.0091(3)
S1	0.0290(6)	0.0329(7)	0.0408(7)	-0.0103(5)	0.0018(6)	0.0033(5)
N1	0.027(2)	0.035(2)	0.044(2)	-0.0094(19)	0.0019(19)	0.0034(18)
N2	0.026(2)	0.029(2)	0.036(2)	-0.0036(17)	0.0035(18)	0.0016(17)
N3	0.036(2)	0.021(2)	0.036(2)	-0.0027(17)	0.0016(19)	-0.0004(17)
C1	0.031(3)	0.022(3)	0.032(3)	0.0009(19)	0.007(2)	0.002(2)
C2	0.040(3)	0.024(3)	0.028(2)	0.005(2)	0.006(2)	0.003(2)
C3	0.042(3)	0.049(4)	0.045(3)	-0.011(3)	0.015(3)	-0.005(3)
C4	0.045(3)	0.023(3)	0.032(3)	0.007(2)	0.001(2)	0.004(2)
C5	0.038(3)	0.040(3)	0.038(3)	-0.011(2)	0.000(2)	0.009(2)
C6	0.039(3)	0.039(3)	0.053(3)	-0.007(3)	-0.004(3)	0.006(2)
C7	0.056(3)	0.034(3)	0.036(3)	-0.001(2)	-0.008(3)	0.000(3)
C8	0.088(5)	0.048(4)	0.034(3)	-0.013(3)	0.012(3)	-0.010(3)
C9	0.070(4)	0.047(4)	0.042(3)	-0.009(3)	0.020(3)	-0.013(3)
N4	0.044(3)	0.067(4)	0.063(3)	-0.003(3)	0.010(3)	0.000(3)
C10	0.039(3)	0.036(3)	0.038(3)	0.001(2)	0.002(2)	0.002(2)
C11	0.042(3)	0.041(3)	0.055(3)	-0.001(3)	0.010(3)	-0.005(3)
Cl1	0.0239(8)	0.0250(9)	0.0423(9)	0	0.0076(7)	0

The Temperature Factor has the Form of Exp(-T) Where
T = 8*(Pi**2)*U*(Sin(Theta)/Lambda)**2 for Isotropic Atoms
T = 2*(Pi**2)*Sumij(h(i)*h(j)*U(i,j)*Astar(i)*Astar(j)), for
Anisotropic Atoms. Astar(i) are Reciprocal Axial Lengths and
h(i) are the Reflection Indices.

Table S6: Bond Distances (Angstrom) of **1.**

Au1	-S1	2.2825(13)	C5	-C6	1.387(7)
Au1	-S1_a	2.2825(13)	C6	-C7	1.378(7)
Br1	-C7	1.905(5)	C7	-C8	1.356(9)
S1	-C1	1.719(5)	C8	-C9	1.390(9)
N1	-C1	1.318(6)	C3	-H3B	0.9800
N2	-N3	1.399(5)	C3	-H3C	0.9800
N2	-C1	1.340(6)	C3	-H3A	0.9800
N3	-C2	1.287(6)	C5	-H5	0.9500
N1	-H1A	0.8800	C6	-H6	0.9500
N1	-H1B	0.8800	C8	-H8	0.9500
N2	-H2	0.8800	C9	-H9	0.9500
N4	-C10	1.127(8)	C10	-C11	1.444(8)
C2	-C3	1.496(7)	C11	-H11A	0.9800
C2	-C4	1.481(7)	C11	-H11B	0.9800
C4	-C5	1.397(7)	C11	-H11C	0.9800
C4	-C9	1.386(7)			

Table S7: Bond Angles (Degrees) of **1.**

S1	-Au1	-S1_a	170.24(6)	C7	-C8	-C9	119.8(5)
Au1	-S1	-C1	109.59(17)	C4	-C9	-C8	120.8(6)
N3	-N2	-C1	116.4(4)	C2	-C3	-H3A	109.00
N2	-N3	-C2	117.6(4)	C2	-C3	-H3B	109.00
H1A	-N1	-H1B	120.00	C2	-C3	-H3C	109.00
C1	-N1	-H1A	120.00	H3A	-C3	-H3B	109.00
C1	-N1	-H1B	120.00	H3A	-C3	-H3C	109.00
N3	-N2	-H2	122.00	H3B	-C3	-H3C	110.00
C1	-N2	-H2	122.00	C4	-C5	-H5	120.00
S1	-C1	-N1	118.2(3)	C6	-C5	-H5	120.00
S1	-C1	-N2	122.5(4)	C5	-C6	-H6	121.00
N1	-C1	-N2	119.2(4)	C7	-C6	-H6	120.00
N3	-C2	-C3	125.7(4)	C7	-C8	-H8	120.00
C3	-C2	-C4	119.2(4)	C9	-C8	-H8	120.00
N3	-C2	-C4	115.1(4)	C4	-C9	-H9	120.00
C2	-C4	-C9	121.6(5)	C8	-C9	-H9	120.00
C5	-C4	-C9	118.2(5)	N4	-C10	-C11	178.6(6)
C2	-C4	-C5	120.2(4)	C10	-C11	-H11A	109.00
C4	-C5	-C6	120.8(5)	C10	-C11	-H11B	109.00
C5	-C6	-C7	119.1(5)	C10	-C11	-H11C	109.00
Br1	-C7	-C6	120.0(4)	H11A	-C11	-H11B	109.00
C6	-C7	-C8	121.3(5)	H11A	-C11	-H11C	109.00
Br1	-C7	-C8	118.7(4)	H11B	-C11	-H11C	110.00

Table S8 Torsion Angles (Degrees) of **1.**

Au1	-S1	-C1	-N1	166.5(3)
Au1	-S1	-C1	-N2	-11.6(4)
C1	-N2	-N3	-C2	-170.6(4)
N3	-N2	-C1	-S1	-178.2(3)
N3	-N2	-C1	-N1	3.7(6)
N2	-N3	-C2	-C3	1.0(7)
N2	-N3	-C2	-C4	-178.6(4)

N3	-C2	-C4	-C5	22.5(7)
N3	-C2	-C4	-C9	-157.0(5)
C3	-C2	-C4	-C5	-157.2(5)
C3	-C2	-C4	-C9	23.4(7)
C2	-C4	-C5	-C6	179.0(5)
C9	-C4	-C5	-C6	-1.5(8)
C2	-C4	-C9	-C8	-179.2(5)
C5	-C4	-C9	-C8	1.3(8)
C4	-C5	-C6	-C7	0.1(8)
C5	-C6	-C7	-Br1	-178.0(4)
C5	-C6	-C7	-C8	1.5(8)
Br1	-C7	-C8	-C9	177.8(4)
C6	-C7	-C8	-C9	-1.7(9)
C7	-C8	-C9	-C4	0.3(9)

Table S9: Contact Distances(Angstrom) of **1.**

Au1	.Cl1	3.3265(17)	Cl1	.H1B_m	2.3700
Au1	.C5_f	4.047(5)	S1	.N3_f	3.362(4)
Au1	.Cl1_c	3.3265(17)	S1	.C2_f	3.684(5)
Au1	.C5_e	4.047(5)	S1	.H11C_d	2.9800
Au1	.H11C_b	3.6300	N1	.N3	2.609(6)
Au1	.H2_a	2.8600	N1	.N4	3.030(7)
Au1	.H11C_d	3.6300	N1	.Cl1_l	3.237(4)
Au1	.H5_e	3.2900	N1	.Cl1_j	3.237(4)
Au1	.H2	2.8600	N2	.Cl1_c	3.242(4)
Au1	.H5_f	3.2900	N2	.Cl1	3.242(4)
Br1	.H3B_g	3.0300	N3	.N1	2.609(6)
Br1	.H6_h	3.0900	N3	.S1_m	3.362(4)
Br1	.H11B_i	3.1200	N4	.N1	3.030(7)
Cl1	.C3	3.516(5)	N1	.H11B_k	2.8700
Cl1	.N1_m	3.237(4)	N2	.H3C	2.3900
Cl1	.N1_v	3.237(4)	N3	.H1A	2.2500
Cl1	.N2	3.242(4)	N3	.H5	2.4800
Cl1	.C3_a	3.516(5)	N4	.H8_p	2.7400
Cl1	.Au1	3.3265(17)	N4	.H3A_q	2.7300
Cl1	.N2_a	3.242(4)	N4	.H1A	2.2800
Cl1	.Au1	3.3265(17)	N4	.H5	2.9200
Cl1	.H11C_d	3.0100	C2	.S1_m	3.684(5)
Cl1	.H1B_v	2.3700	C3	.Cl1_c	3.516(5)
Cl1	.H3C_a	2.9600	C3	.Cl1	3.516(5)
Cl1	.H2	2.5600	C5	.Au1_m	4.047(5)
Cl1	.H3C	2.9600	C5	.Au1_g	4.047(5)
Cl1	.H11C_b	3.0100	C1	.H11B_k	2.9900
Cl1	.H2_a	2.5600	C3	.H2	2.5000
C3	.H9	2.6600	H3C	.Cl1	2.9600
C5	.H11A_n	3.0600	H5	.N4	2.9200
C6	.H11A_n	2.9300	H5	.N3	2.4800
C7	.H11A_n	3.0200	H5	.Au1_m	3.2900
C9	.H3B	2.7200	H5	.Au1_g	3.2900
H1A	.N4	2.2800	H6	.Br1_h	3.0900
H1A	.N3	2.2500	H8	.N4_o	2.7400
H1B	.Cl1_j	2.3700	H9	.C3	2.6600
H1B	.Cl1_l	2.3700	H9	.H3B	2.1300

H2	.Cl1_c	2.5600	H11A	.C5_q	3.0600
H2	.Au1	2.8600	H11A	.C7_q	3.0200
H2	.C3	2.5000	H11A	.C6_q	2.9300
H2	.H3C	1.8400	H11B	.N1_g	2.8700
H2	.Cl1	2.5600	H11B	.Br1_h	3.1200
H3A	.N4_n	2.7300	H11B	.C1_g	2.9900
H3B	.Br1_e	3.0300	H11C	.Au1_r	3.6300
H3B	.H9	2.1300	H11C	.Cl1_s	3.0100
H3B	.C9	2.7200	H11C	.Cl1_u	3.0100
H3C	.H2	1.8400	H11C	.S1_t	2.9800
H3C	.Cl1_c	2.9600	H11C	.Au1_t	3.6300
H3C	.N2	2.3900			

Table S10: Hydrogen Bonds (Angstrom, Deg) of **1.**

N1 -- H1A .. N3	0.8800	2.2500	2.609(6)	104.00	.
N1 -- H1A .. N4	0.8800	2.2800	3.030(7)	144.00	.
N1 -- H1B .. Cl1	0.8800	2.3700	3.237(4)	168.00	5_545
N2 -- H2 .. Cl1	0.8800	2.5600	3.242(4)	135.00	.
C3 -- H3C .. N2	0.9800	2.3900	2.809(6)	105.00	.

Translation of Symmetry Code to Equiv.Pos

a =[2555.00] = -x,y,1/2-z; **b** =[1455.00] = -1+x,y,z

c =[2555.00] = -x,y,1/2-z; **d** =[2655.00] = 1-x,y,1/2-z

e =[5445.00] = -1/2+x,-1/2+y,z; **f** =[6545.00] = 1/2-x,-1/2+y,1/2-z

g =[5555.00] = 1/2+x,1/2+y,z; **h** =[7666.00] = 3/2-x,3/2-y,1-z

i =[7666.00] = 3/2-x,3/2-y,1-z; **j** =[5545.00] = 1/2+x,-1/2+y,z

k =[5445.00] = -1/2+x,-1/2+y,z; **l** =[6545.00] = 1/2-x,-1/2+y,1/2-z

m =[6555.00] = 1/2-x,1/2+y,1/2-z; **n** =[5455.00] = -1/2+x,1/2+y,z

o =[3666.00] = 1-x,1-y,1-z; **p** =[3666.00] = 1-x,1-y,1-z

r =[1655.00] = 1+x,y,z; **s** =[1655.00] = 1+x,y,z

t =[2655.00] = 1-x,y,1/2-z; **u** =[2655.00] = 1-x,y,1/2-z

v =[5455.00] = -1/2+x,1/2+y,z

Table S11: Crystal Data and Details of the Structure Determination of **2.**

Crystal Data

Formula	C18 H18 N6 S2 AU CL4+, 2(C2 H3 N1), CL-		
Formula Weight			838.83
Crystal System			Monoclinic
Space group		C2/c	(No. 15)
a, b, c [Angstrom]	11.776(2)	10.658(2)	24.515(5)
alpha, beta, gamma [deg]	90	96.79(3)	90
V [Ang**3]			3055.3(10)
Z			4
D(calc) [g/cm**3]			1.824
Mu(MoKa) [/mm]			5.417

F(000)	1632
Crystal Size [mm]	0.05 x 0.05 x 0.05
Data Collection	
Temperature (K)	173
Radiation [Angstrom]	MoKa 0.71073
Theta Min-Max [Deg]	2.6, 25.7
Dataset	-14: 13 ; -11: 12 ; -28: 29
Tot., Uniq. Data, R(int)	9300, 2889, 0.040
Observed data [I > 2.0 sigma(I)]	2377
Refinement	
Nref, Npar	2889, 176
R, wR2, S	0.0330, 0.0702, 1.07
w = 1/[\s^2^(Fo^2^)+(0.0275P)^2^+5.3451P] where P=(Fo^2^+2Fc^2^)/3	
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. Resd. Dens. [e/Ang^3]	-1.18, 1.74

Table S12: Final Coordinates and Equivalent Isotropic Displacement Parameters of the non-Hydrogen atoms of **2.**

Atom	x	y	z	U(eq) [Ang^2]
Au1	0	0.12628(3)	1/4	0.0316(1)
Cl2	0.65645(11)	0.62732(13)	0.41695(6)	0.0473(4)
Cl3	0.58445(14)	0.76839(14)	0.52138(6)	0.0541(5)
S1	0.19017(10)	0.10699(12)	0.24170(5)	0.0358(4)
N1	0.3778(3)	0.1844(4)	0.29922(17)	0.0367(12)
N2	0.2193(3)	0.3001(4)	0.31238(15)	0.0292(12)
N3	0.2914(3)	0.3730(3)	0.34846(15)	0.0262(11)
C1	0.2677(4)	0.2062(4)	0.28792(18)	0.0280(14)
C2	0.2468(4)	0.4475(4)	0.38128(18)	0.0282(16)
C3	0.1217(4)	0.4602(5)	0.3867(2)	0.0368(17)
C4	0.3300(4)	0.5253(4)	0.41636(18)	0.0292(16)
C5	0.4409(4)	0.5408(4)	0.40332(19)	0.0309(17)
C6	0.5194(4)	0.6133(4)	0.4350(2)	0.0329(17)
C7	0.4886(4)	0.6733(5)	0.4810(2)	0.0371(17)
C8	0.3798(4)	0.6578(5)	0.4955(2)	0.0388(17)
C9	0.3001(4)	0.5848(5)	0.4631(2)	0.0356(17)
N4	0.6020(4)	0.2956(5)	0.3520(2)	0.0539(17)
C10	0.6946(5)	0.3275(5)	0.3544(2)	0.0413(17)
C11	0.8127(4)	0.3690(5)	0.3590(3)	0.048(2
Cl1	0	0.44239(15)	1/4	0.0295(5)

U(eq) = 1/3 of the trace of the orthogonalized U Tensor

Table S13: Hydrogen Atom Positions and Isotropic Displacement Parameters of **2.**

Atom	x	y	z	U(iso) [Ang^2]
H1A	0.41970	0.23200	0.32300	0.0440
H1B	0.40960	0.12210	0.28300	0.0440
H2	0.14540	0.31530	0.30600	0.0350
H3A	0.09620	0.54510	0.37590	0.0550
H3B	0.10890	0.44490	0.42490	0.0550

H3C	0.07850	0.39890	0.36270	0.0550
H5	0.46290	0.50020	0.37170	0.0370
H8	0.35920	0.69710	0.52770	0.0470
H9	0.22500	0.57570	0.47300	0.0430
H11A	0.86260	0.30220	0.37550	0.0730
H11B	0.82190	0.44400	0.38220	0.0730
H11C	0.83330	0.38880	0.32240	0.0730

The Temperature Factor has the Form of Exp(-T) Where
T = 8*(Pi**2)*U*(Sin(Theta)/Lambda)**2 for Isotropic Atoms

Table S14: (An)isotropic Displacement Parameters of **2.**

Atom	U(1,1) or U	U(2,2)	U(3,3)	U(2,3)	U(1,3)	U(1,2)
Au1	0.0260(2)	0.0308(2)	0.0370(2)	0	-0.0004(1)	0
Cl2	0.0367(7)	0.0489(8)	0.0561(8)	0.0022(7)	0.0044(6)	-0.0141(7)
Cl3	0.0644(10)	0.0441(8)	0.0487(8)	-0.0047(7)	-0.0145(7)	-0.0156(7)
S1	0.0270(6)	0.0380(7)	0.0414(7)	-0.0137(6)	0.0004(5)	0.0019(6)
N1	0.024(2)	0.039(2)	0.047(2)	-0.012(2)	0.0034(19)	0.0063(19)
N2	0.022(2)	0.033(2)	0.032(2)	-0.0069(19)	0.0008(17)	-0.0009(18)
N3	0.0249(19)	0.025(2)	0.0283(19)	0.0003(18)	0.0016(16)	0.0007(18)
C1	0.024(2)	0.029(3)	0.031(2)	0.000(2)	0.003(2)	0.000(2)
C2	0.030(3)	0.029(3)	0.025(2)	0.003(2)	0.001(2)	0.003(2)
C3	0.031(3)	0.038(3)	0.042(3)	-0.008(2)	0.007(2)	0.004(2)
C4	0.030(3)	0.027(3)	0.030(2)	0.003(2)	0.001(2)	0.004(2)
C5	0.034(3)	0.026(3)	0.032(3)	0.003(2)	0.001(2)	0.001(2)
C6	0.032(3)	0.029(3)	0.037(3)	0.006(2)	0.001(2)	-0.003(2)
C7	0.041(3)	0.031(3)	0.036(3)	0.000(2)	-0.009(2)	-0.001(2)
C8	0.045(3)	0.038(3)	0.033(3)	-0.005(2)	0.003(2)	0.004(2)
C9	0.034(3)	0.037(3)	0.035(3)	-0.004(2)	0.001(2)	0.001(2)
N4	0.034(3)	0.060(3)	0.069(3)	-0.013(3)	0.011(2)	-0.004(2)
C10	0.041(3)	0.042(3)	0.042(3)	-0.005(3)	0.009(3)	0.004(3)
C11	0.032(3)	0.053(4)	0.062(4)	-0.003(3)	0.013(3)	-0.001(3)
Cl1	0.0217(8)	0.0292(9)	0.0377(9)	0	0.0040(7)	0

The Temperature Factor has the Form of Exp(-T) Where
T = 8*(Pi**2)*U*(Sin(Theta)/Lambda)**2 for Isotropic Atoms
T = 2*(Pi**2)*Sumij(h(i)*h(j)*U(i,j)*Astar(i)*Astar(j)), for
Anisotropic Atoms. Astar(i) are Reciprocal Axial Lengths and
h(i) are the Reflection Indices.

Table S15: Bond Distances (Angstrom) of **2.**

Au1	-S1	2.2818(13)	C4	-C5	1.391(7)
Au1	-S1_a	2.2818(13)	C5	-C6	1.373(7)
Cl2	-C6	1.730(5)	C6	-C7	1.382(7)
Cl3	-C7	1.737(5)	C7	-C8	1.380(7)

S1	-C1	1.729(5)	C8	-C9	1.393(7)
N1	-C1	1.314(6)	C3	-H3B	0.9800
N2	-N3	1.389(5)	C3	-H3C	0.9800
N2	-C1	1.329(6)	C3	-H3A	0.9800
N3	-C2	1.286(6)	C5	-H5	0.9500
N1	-H1A	0.8800	C8	-H8	0.9500
N1	-H1B	0.8800	C9	-H9	0.9500
N2	-H2	0.8800	C10	-C11	1.451(8)
N4	-C10	1.137(8)	C11	-H11A	0.9800
C2	-C4	1.479(6)	C11	-H11B	0.9800
C2	-C3	1.501(7)	C11	-H11C	0.9800
C4	-C9	1.391(7)			

Table S16: Bond Angles (Degrees) of **2**.

S1	-Au1	-S1_a	169.66(6)	C6	-C7	-C8	119.8(5)
Au1	-S1	-C1	109.52(17)	Cl3	-C7	-C8	118.9(4)
N3	-N2	-C1	116.5(4)	C7	-C8	-C9	120.2(5)
N2	-N3	-C2	118.7(4)	C4	-C9	-C8	120.4(4)
C1	-N1	-H1A	120.00	C2	-C3	-H3A	109.00
C1	-N1	-H1B	120.00	C2	-C3	-H3B	109.00
H1A	-N1	-H1B	120.00	C2	-C3	-H3C	109.00
C1	-N2	-H2	122.00	H3A	-C3	-H3B	110.00
N3	-N2	-H2	122.00	H3A	-C3	-H3C	109.00
S1	-C1	-N2	122.3(4)	H3B	-C3	-H3C	110.00
N1	-C1	-N2	120.2(4)	C4	-C5	-H5	119.00
S1	-C1	-N1	117.5(3)	C6	-C5	-H5	119.00
N3	-C2	-C3	126.1(4)	C7	-C8	-H8	120.00
N3	-C2	-C4	114.7(4)	C9	-C8	-H8	120.00
C3	-C2	-C4	119.2(4)	C4	-C9	-H9	120.00
C5	-C4	-C9	118.1(4)	C8	-C9	-H9	120.00
C2	-C4	-C9	121.3(4)	N4	-C10	-C11	178.5(6)
C2	-C4	-C5	120.6(4)	C10	-C11	-H11A	109.00
C4	-C5	-C6	121.6(4)	C10	-C11	-H11B	109.00
Cl2	-C6	-C5	119.4(4)	C10	-C11	-H11C	109.00
C5	-C6	-C7	119.9(4)	H11A	-C11	-H11B	109.00
Cl2	-C6	-C7	120.8(4)	H11A	-C11	-H11C	109.00
Cl3	-C7	-C6	121.3(4)	H11B	-C11	-H11C	109.00

Table S17: Torsion Angles (Degrees) in **2.**

Au1	-S1	-C1	-N1	162.4(3)
Au1	-S1	-C1	-N2	-16.3(4)
C1	-N2	-N3	-C2	-166.0(4)
N3	-N2	-C1	-S1	-179.8(3)
N3	-N2	-C1	-N1	1.5(6)
N2	-N3	-C2	-C3	3.1(6)
N2	-N3	-C2	-C4	-177.4(4)
N3	-C2	-C4	-C5	17.1(6)
N3	-C2	-C4	-C9	-162.9(4)
C3	-C2	-C4	-C5	-163.3(4)
C3	-C2	-C4	-C9	16.7(6)
C2	-C4	-C5	-C6	179.5(4)

C9	-C4	-C5	-C6	-0.5(7)
C2	-C4	-C9	-C8	-179.9(4)
C5	-C4	-C9	-C8	0.1(7)
C4	-C5	-C6	-Cl2	179.3(4)
C4	-C5	-C6	-C7	-0.2(7)
Cl2	-C6	-C7	-Cl3	1.8(6)
Cl2	-C6	-C7	-C8	-178.1(4)
C5	-C6	-C7	-Cl3	-178.7(4)
C5	-C6	-C7	-C8	1.4(7)
Cl3	-C7	-C8	-C9	178.3(4)
C6	-C7	-C8	-C9	-1.8(8)
C7	-C8	-C9	-C4	1.0(8)

Table S18: Contact Distances (Angstrom) in **2.**

Au1	.Cl1	3.3691(18)	Cl1	.H3C_a	2.8500
Au1	.C5_c	4.008(5)	Cl1	.H2	2.4700
Au1	.Cl1_b	3.3691(18)	Cl1	.H3C	2.8500
Au1	.C5_d	4.008(5)	Cl1	.H1B_k	2.3800
Au1	.H2	2.8800	Cl2	.H11B	2.9500
Au1	.H5_c	3.3500	Cl3	.H3B_e	3.0600
Au1	.H2_a	2.8800	S1	.C10_h	3.697(5)
Au1	.H5_d	3.3500	S1	.C2_d	3.614(5)
Cl1	.N1_t	3.254(4)	S1	.N3_d	3.356(4)
Cl1	.N1_k	3.254(4)	N1	.N3	2.612(5)
Cl1	.Au1	3.3691(18)	N1	.N4	3.040(6)
Cl1	.Au1	3.3691(18)	N1	.Cl1_j	3.254(4)
Cl1	.N2	3.221(4)	N1	.Cl1_i	3.254(4)
Cl1	.C3	3.491(5)	N2	.Cl1	3.221(4)
Cl1	.N2_a	3.221(4)	N2	.Cl2_c	3.311(4)
Cl1	.C3_a	3.491(5)	N2	.Cl1_b	3.221(4)
Cl2	.Cl3_f	3.426(2)	N3	.N1	2.612(5)
Cl2	.C10	3.595(5)	N3	.S1_k	3.356(4)
Cl2	.Cl3	3.170(2)	N4	.N1	3.040(6)
Cl2	.C3_e	3.638(6)	N2	.H3C	2.4200
Cl2	.N2_e	3.311(4)	N3	.H5	2.4400
Cl3	.C4_g	3.575(5)	N3	.H1A	2.2700
Cl3	.Cl2	3.170(2)	N4	.H8_g	2.9300
Cl3	.Cl2_f	3.426(2)	N4	.H1A	2.2800
Cl1	.H1B_t	2.3800	N4	.H5	2.8000
Cl1	.H11C_h	2.8600	N4	.H3A_o	2.7400
Cl1	.H11C_s	2.8600	C2	.S1_k	3.614(5)
Cl1	.H2_a	2.4700	C3	.Cl1_b	3.491(5)

Table S19: Contact Distances (Angstrom) in **2**. (continued)

C3	.Cl2_c	3.638(6)	H2	.Au1	2.8800
C3	.Cl1	3.491(5)	H3A	.C9	3.0500
C4	.Cl3_g	3.575(5)	H3A	.N4_l	2.7400
C5	.Au1_e	4.008(5)	H3B	.C9	2.7700
C5	.Au1_k	4.008(5)	H3B	.H9	2.2000
C6	.C8_g	3.490(7)	H3B	.Cl3_c	3.0600
C8	.C6_g	3.490(7)	H3C	.Cl1	2.8500

C10	.Cl2	3.595(5)	H3C	.N2	2.4200
C10	.S1_p	3.697(5)	H3C	.H2	1.9000
C3	.H2	2.5500	H3C	.Cl1_b	2.8500
C3	.H9	2.6200	H5	.N4	2.8000
C5	.H11A_l	2.9900	H5	.Au1_e	3.3500
C6	.H11A_l	2.9900	H5	.Au1_k	3.3500
C9	.H3B	2.7700	H5	.N3	2.4400
C9	.H3A	3.0500	H8	.N4_n	2.9300
C9	.H8_m	3.0100	H8	.C9_m	3.0100
C10	.H8_g	3.0400	H8	.C10_n	3.0400
H1A	.N4	2.2800	H9	.H3B	2.2000
H1A	.N3	2.2700	H9	.C3	2.6200
H1B	.Cl1_i	2.3800	H11A	.C5_o	2.9900
H1B	.Cl1_j	2.3800	H11A	.C6_o	2.9900
H2	.Cl1	2.4700	H11B	.Cl2	2.9500
H2	.H3C	1.9000	H11C	.Cl1_q	2.8600
H2	.Cl1_b	2.4700	H11C	.Cl1_r	2.8600
H2	.C3	2.5500			

Table S20: Hydrogen Bonds (Angstrom, Deg) in **2.**

N1 -- H1A .. N3	0.8800	2.2700	2.612(5)	103.00	.
N1 -- H1A .. N4	0.8800	2.2800	3.040(6)	144.00	.
N1 -- H1B .. Cl1	0.8800	2.3800	3.254(4)	173.00	5_545
N2 -- H2 .. Cl1	0.8800	2.4700	3.221(4)	144.00	.
C3 -- H3C .. N2	0.9800	2.4200	2.837(6)	105.00	.

Translation of Symmetry Code to Equiv.Pos

a =[2555.00] = -x,y,1/2-z; b =[2555.00] = -x,y,1/2-z
c =[5445.00] = -1/2+x,-1/2+y,z; d =[6545.00] = 1/2-x,-1/2+y,1/2-z
e =[5555.00] = 1/2+x,1/2+y,z; f =[7666.00] = 3/2-x,3/2-y,1-z
g =[3666.00] = 1-x,1-y,1-z; h =[2655.00] = 1-x,y,1/2-z
i =[5545.00] = 1/2+x,-1/2+y,z; j =[6545.00] = 1/2-x,-1/2+y,1/2-z
k =[6555.00] = 1/2-x,1/2+y,1/2-z; l =[5455.00] = -1/2+x,1/2+y,z
m =[7566.00] = 1/2-x,3/2-y,1-z; n =[3666.00] = 1-x,1-y,1-z
p =[2655.00] = 1-x,y,1/2-z; q =[1655.00] = 1+x,y,z
r =[2655.00] = 1-x,y,1/2-z; s =[1455.00] = -1+x,y,z
t =[5455.00] = -1/2+x,1/2+y,z

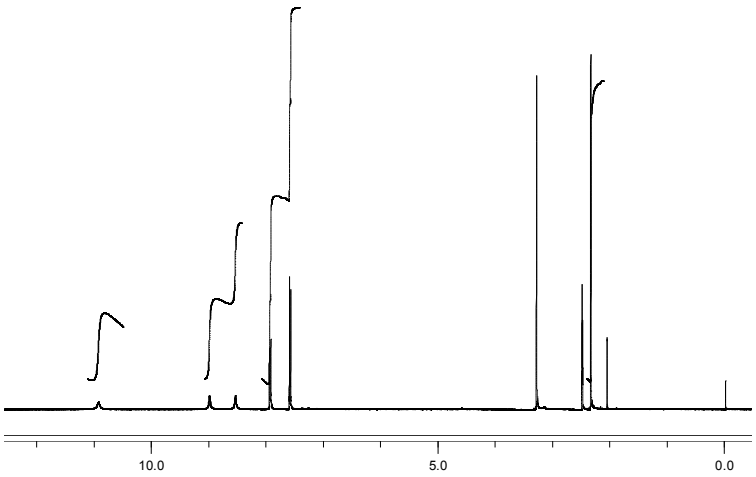

Figure S4: NMR spectrum of **1.**

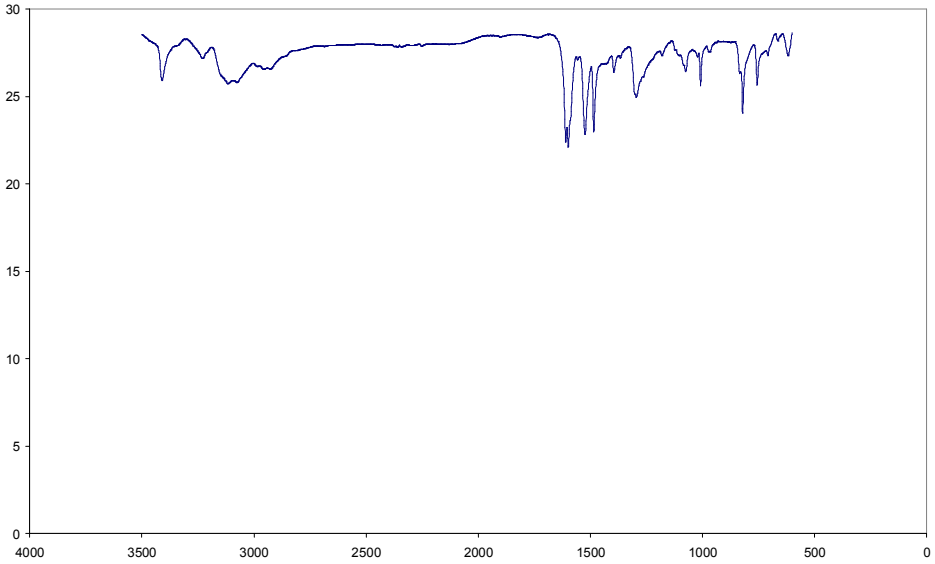

Figure S4: Infrared spectrum of **1**.

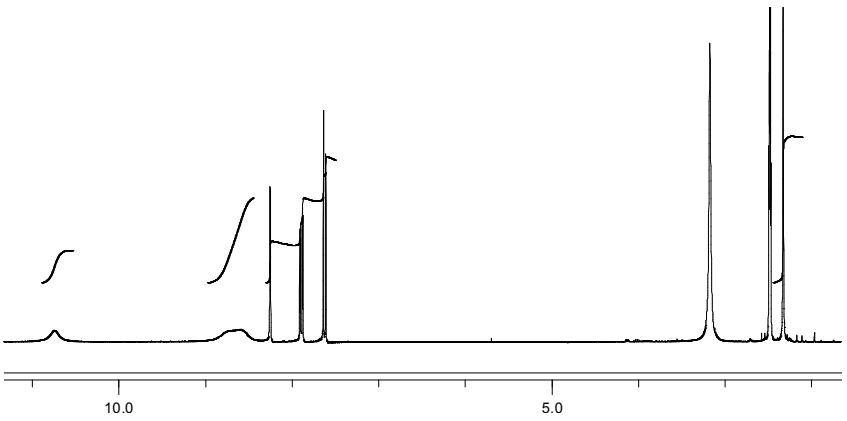

Figure S5: ^{1}H NMR spectrum of **2.**

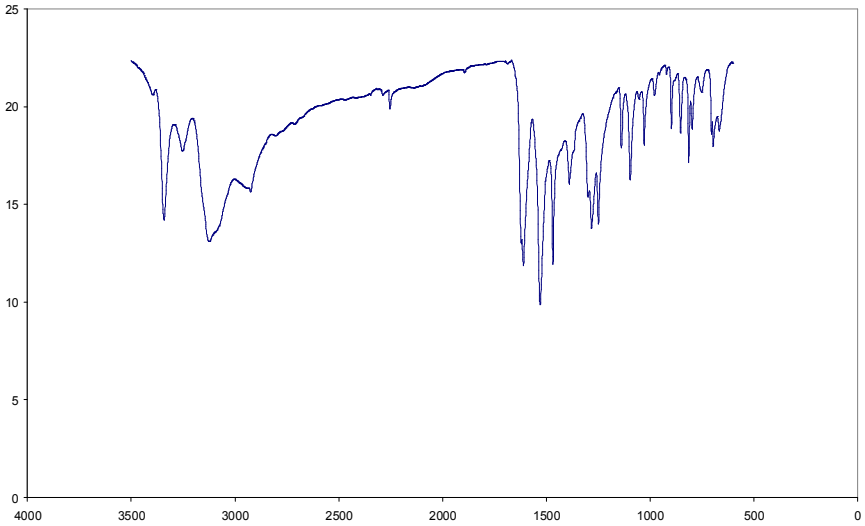

Figure S6: Infrared spectrum of **2**.

References

1. COLLECT, *Data Collection Software*, Nonius, Delft, The Netherlands, 1999.
2. Z. Otwinowski, W. Minor, *DENZO and SCALEPACK*. In International Tables of Crystallography, Vol F. ed.: M.G. Rossman, E. Arnold, Kluwer, Dordrecht, 2000.
3. G.M. Sheldrick, *SHELXS-97 and SHELXL-97 Programs for crystal structure determination and refinement.* University of Gottingen, 1997.
4. L.J. Barbour, *J. Supramol. Chem*. 2000, **1**, 86.
5. A.L. Spek, *J. Appl. Crystallogr*. 2003. **36**. 7.
6. Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. J. *Appl. Cryst.*, 2008, **41**, 466-470.