Electronic Supplementary Information for Dalton Transactions

Novel Cr^{III} dinuclear complexes supported by salicyloylhydrazono dithiolane and dithiane ligands : synthesis, stability, crystal structures and magnetic properties

Nicolas Clément,[a] Clément Toussaint,[a] Guillaume Rogez,[b] Claudia Loose,[c] Jens Kortus,[c] Lydia Brelot[d], Sylvie Choua,[e] Samuel Dagorne,[a] Philippe Turek,[e] and Richard Welter[*a]*

[a]Laboratoire DECOMET, UMR-CNRS 7177, Université de Strasbourg, 4, rue Blaise Pascal, 67070 Strasbourg Cedex, France. Fax: +33 90 24 12 29; Tel: +33 90 24 15 93;

[b] I.P.C.M.S., UMR-CNRS 7504, Groupe des Matériaux Inorganiques, Université de Strasbourg, 23 Rue du Loess, BP 43, F-67034 Strasbourg Cedex 2, France.

[c] Institut für Theoretische Physik, TU Bergakademie Freiberg, Leipziger Str. 23, D-09599 Freiberg, Germany

[d] Service de Radiocristallographie, UMR-CNRS 7177, Université de Strasbourg, 4, rue Blaise Pascal, 67070 Strasbourg Cedex, France.

[e] Laboratoire POMAM, UMR 7177 CNRS, Université de Strasbourg, 1, rue Blaise Pascal, 67008 Strasbourg Cedex, France.

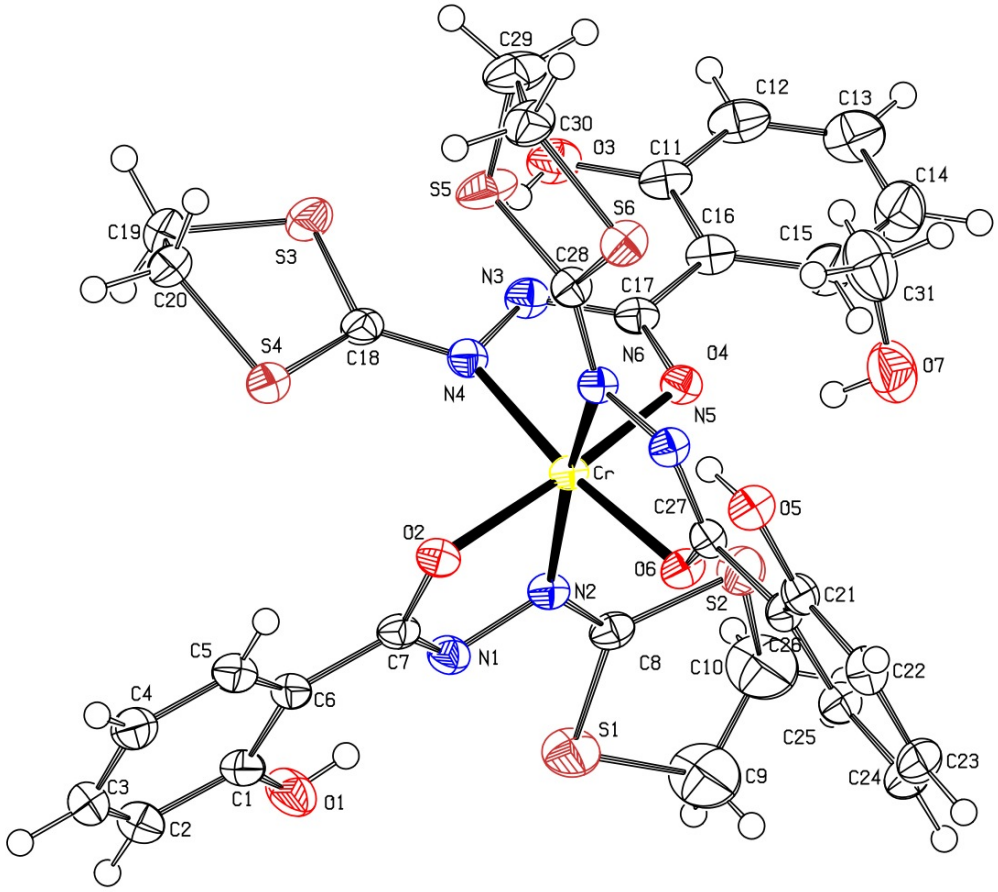

Figure S1 : ORTEP view of complex **1a**, MeOH with full labeling scheme.
The ellipsoids enclose 50% of the electronic density.

Table S1 : Hydrogen bonds detected* in complex **1a**, MeOH.

Type	Donor--H...Acceptor	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
Intra	**O1--H1O…N1**	**0.79(5)**	**1.89(5)**	**2.565(3)**	**144(5)**
Intra	**O3--H3O…N3**	**0.76(5)**	**1.94(5)**	**2.591(3)**	**143(5)**
Intra	**O5--H5O…N5**	**0.89(4)**	**1.80(3)**	**2.590(3)**	**147(4)**
Solv.	*O7--H7...O4*	*0.8398*	*2.1033*	*2.899(3)*	*157.90*
Inter.	C9--H9B…O3$1	0.9900	2.3817	3.321(5)	158.23
Inter.	C19—H19A...O7$4	0.9901	2.4851	3.313(4)	140.94
Inter.	C20—H20B…O1$2	0.9895	2.5418	3.303(4)	133.59
Inter.	C22—H22…O2$3	0.9508	2.4602	3.383(3)	163.54

Equivalent position codes : $1 = -1+x, y, z ; $2 = 1+x, y, z ; $3 = -x, -y, 2-z ; $4 = x, 1+y, z

* Spek, A. L., PLATON software, J. Appl. Cryst., 2003, 36, 7.27

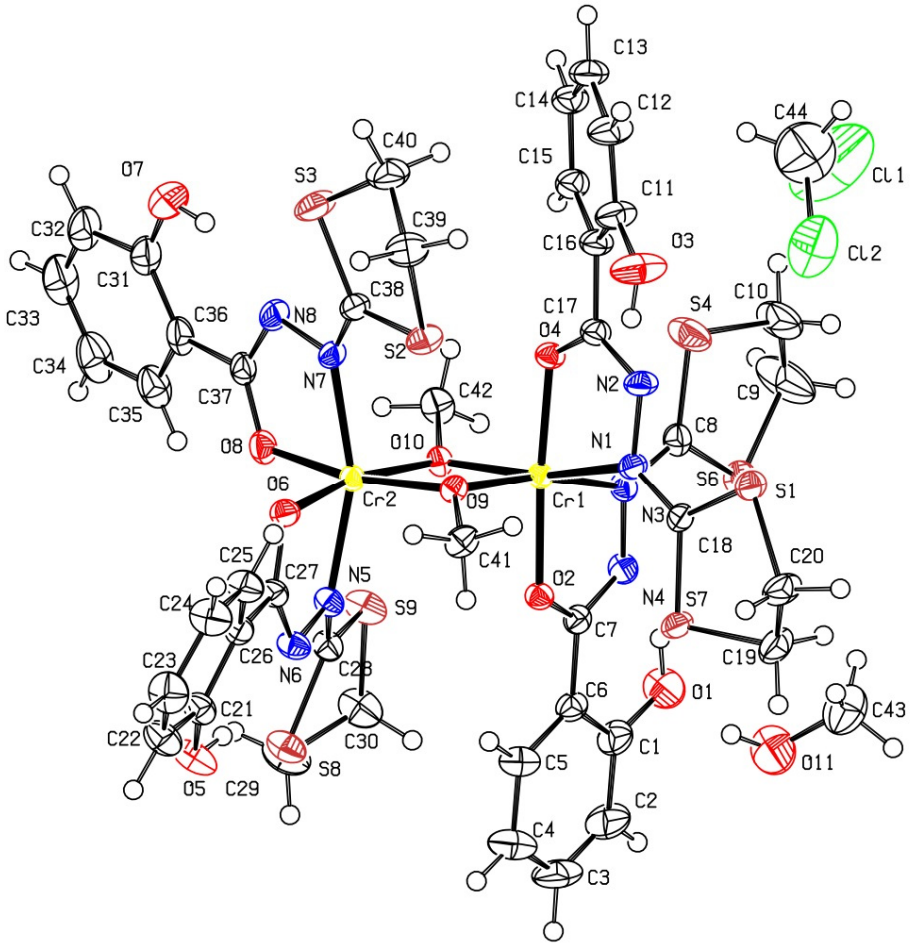

Figure S2 : ORTEP view of complex **2a,** CH_2Cl_2,MeOH with full labeling scheme. The ellipsoids enclose 50% of the electronic density.

Table S2 : Main hydrogen bonds detected* in complex **2a,** CH_2Cl_2,MeOH

Type	*Donor--H...Acceptor*	*D-H (Å)*	*H...A (Å)*	*D...A (Å)*	*D-H...A (°)*
Intra	**O1—HO1...N4**	**0.8407**	**1.8349**	**2.572(4)**	**145.52**
Intra	**O3—HO3...N2**	**0.8396**	**1.9731**	**2.658(4)**	**138.14**
Intra	**O5—HO5...N6**	**0.8401**	**1.9067**	**2.636(4)**	**144.54**
Intra	**O7--H7...N8**	**0.8403**	**1.8630**	**2.590(4)**	**143.92**
Intra	O1—HO1...S6	0.8407	2.8687	3.582(3)	143.86
Intra	O7--H7...S3	0.8403	2.8362	3.576(4)	147.93
Solv.	O11—H11...O1	0.8383	2.0076	2.806(4)	158.83
Inter	C19—H19A...O6$1	0.9905	2.5380	3.303(4)	133.86
Inter	C20—H20A…O3$2	0.9903	2.5046	3.264(5)	133.31
Inter	C22—H22...O8$3	0.9508	2.4960	3.317(4)	144.58
Inter	C25—H25...S7$4	0.9488	2.8163	3.494(3)	129.14

Equivalent position codes : $1= 3/2-x,1/2+y,3/2-z ; $2= 2-x,-y,2-z ; $3= 1-x,-y,1-z ; $4= 3/2-x,-1/2+y,3/2-z

* Spek, A. L., PLATON software, J. Appl. Cryst., 2003, 36, 7.27

Table S3 : Main CH-π interactions* in complex **2a,** CH_2Cl_2,MeOH.

Type	*X—H(I) →Ring*	*H..Centroid (Å)*	*X-H..Centroid (°)*	*X..Centroid (Å)*
Intra	**C30--H30B→(C1/C6)**	**2.8605**	**159.18**	**3.802(5)**
Intra	**C39--H39A→(C11/C16)**	**2.6551**	**157.30**	**3.558(4)**
Inter	C13--H13→(C31/C36)$5	2.7396	134.11	3.469(4)
Inter	C30--H30A→(C31/C36)$6	3.2841	133.44	4.030(5)
Solv.	C44--H44A→(C11/C16)	2.5577	150.25	3.451(9)

Equivalent position codes : $5 = 1/2+x,-1/2-y,1/2+z; $6 = 1/2-x,1/2+y,3/2-z

* Spek, A. L., PLATON software, J. Appl. Cryst., 2003, 36, 7.27

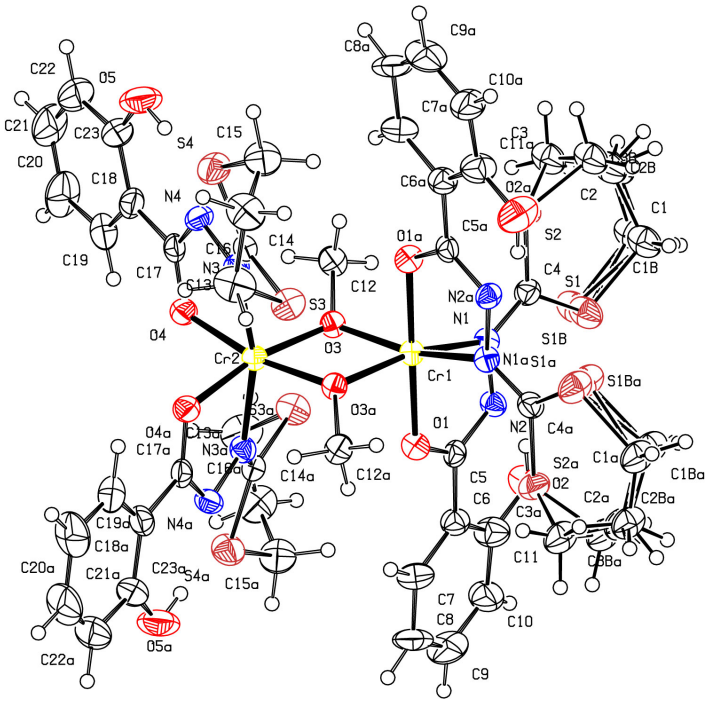

Figure S3 : ORTEP view of complex **2b** with full labeling scheme.
The ellipsoids enclose 50% of the electronic density.
Symmetry code for equivalent position : a = -x-1, -y+2, z

Table S4 : Main hydrogen bonds detected* in complex **2b**.

Type	*Donor--H...Acceptor*	*D-H (Å)*	*H...A (Å)*	*D...A (Å)*	*D-H...A (°)*
Intra	**O2—H2...N2**	**0.8400**	**1.8507**	**2.5911(4)**	**146.18**
Intra	**O5—H5...N4**	**0.8400**	**1.8568**	**2.5949(4)**	**145.81**
Inter	C2—H2B...O2$1	0.9900	2.5790	3.227(3)	122.99
Inter	C2—H2B1...O2$1	0.9776	2.5346	3.227(3)	127.72
Intra	C12—H12A...O1$2	0.9800	2.5115	2.981(4)	109.16
Intra	C12—H12C…O4	0.9800	2.5809	3.115(4)	114.30
Intra	C19—H19...O4	0.9508	2.4485	2.784(4)	100.59
Inter	C20—H20...S2$3	0.9500	2.8286	3.626(4)	142.11

Equivalent position codes : $1= -x,1-y,z ; $2= -x,2-y,z ; $3= x,-1/2+y,-1/2+z.

* Spek, A. L., PLATON software, J. Appl. Cryst., 2003, 36, 7.27

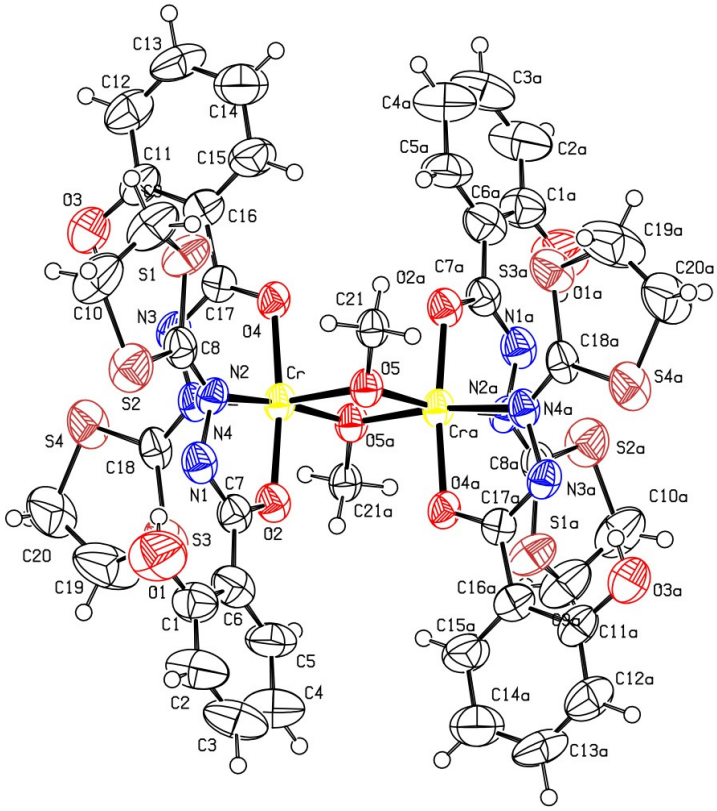

Figure S4 : ORTEP view of complex **2a'** with labeling scheme.

The ellipsoids enclose 50% of the electronic density.

Table S6 : Hydrogen bonds detected* in complex **2a'**

Type	*Donor--H...Acceptor*	*D-H (Å)*	*H...A (Å)*	*D...A (Å)*	*D-H...A (°)*
Intra	**O1--H1…N1**	**0.8397**	**1.8588**	**2.605(7)**	**147.34**
Intra	**O3--H3O…N3**	**0.8389**	**1.8436**	**2.587(6)**	**146.92**
Intra	O1--H1…S2	0.8397	2.8459	3.568(6)	145.27
Intra	C21--H21C…O2$2	0.9790	2.5735	3.095(7)	13.35
Inter	C9--H9A…O3$1	0.9909	2.4881	3.347(7)	144.87

Equivalent position codes : $2 = 3/2-x,1/2-y,-z ; $1 = x,-y,-1/2+z

* Spek, A. L., PLATON software, J. Appl. Cryst., 2003, 36, 7.27

Table S7 : Main CH-π interactions* in complex **2a'**.

Type	*X--H(I)→Ring*	*H..Centroid (Å)*	*X-H..Centroid (°)*	*X..Centroid (Å)*
Inter	C10-H10A→(C1/C6)$1	3.0158	136.90	3.798(10)
Inter	C19-H19A→(C1/C6)$2	3.0530	159.86	3.998(11)
Inter	C19-H19B→(C11/C16)$3	3.2757	144.80	4.124(12)
Inter	C20-H20A→(Cr/O4/N4)$3	3.0589	108.84	3.507(9)
Inter	C20-H20B→(Cr/O2/N2)$2	3.1887	136.29	3.963(7)
Inter	C20-H20B→(Cr/N3/N4)$3	3.0268	111.12	3.507(9)

Equivalent position codes : $1 = 3/2-x,-1/2-y,-z; $2 = x,-y,1/2+z; $3 = 3/2-x,-1/2+y,1/2-z

* Spek, A. L., PLATON software, J. Appl. Cryst., 2003, 36, 7.27

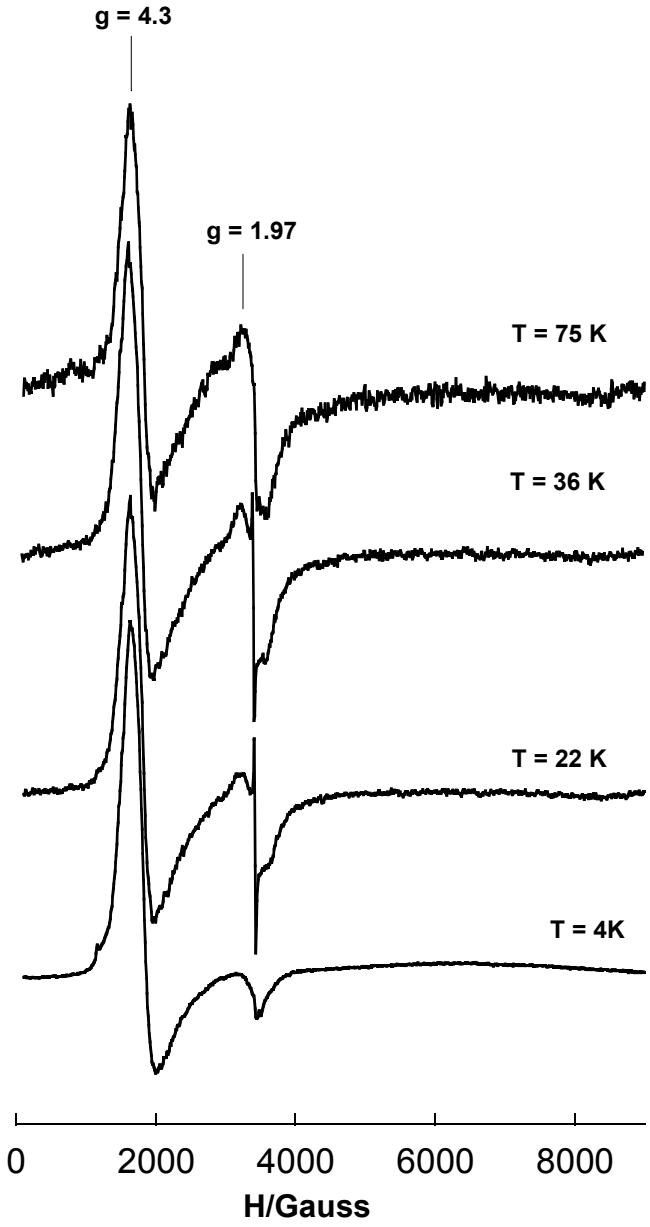

Figure S5: Frozen EPR spectrum of **1a** measured at 4, 22, 36 and 75

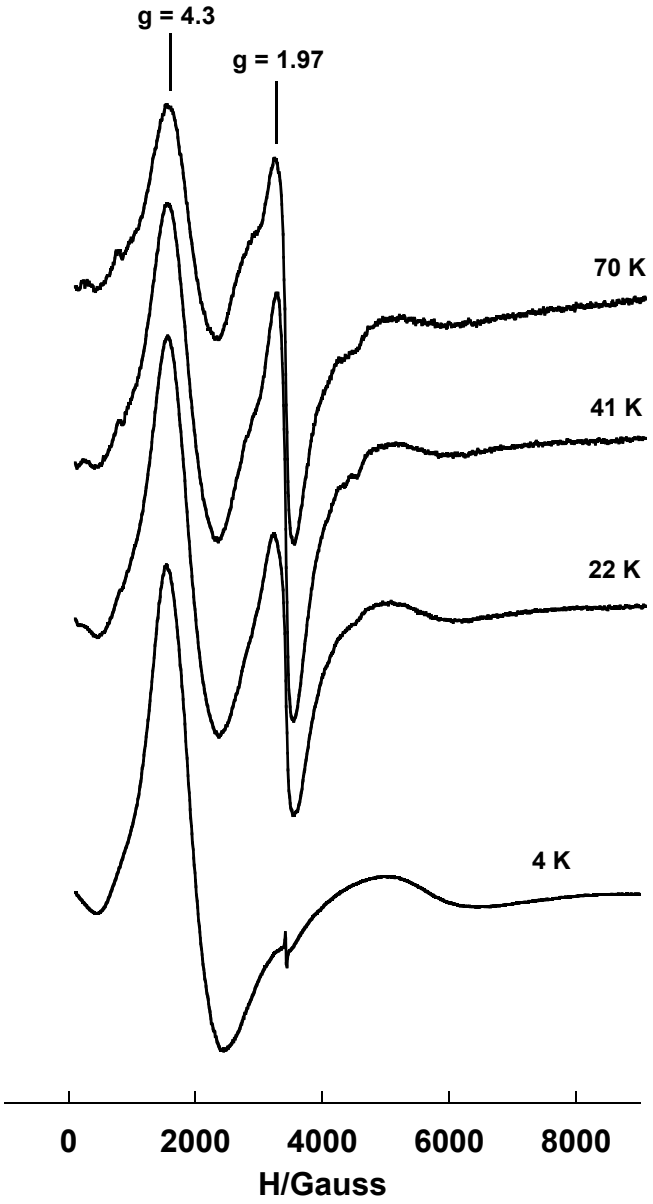

Figure S6: Powder EPR spectrum of **1a** measured at 4, 22, 41 and 70 K

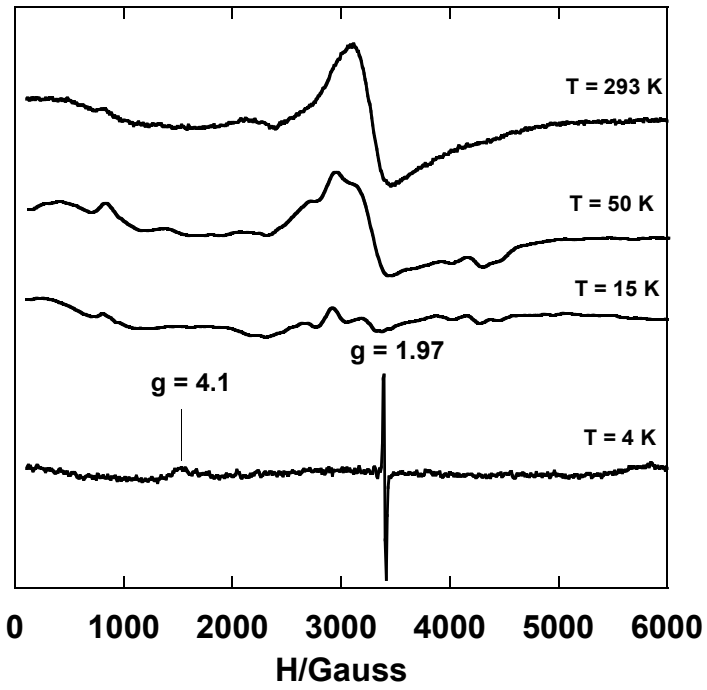

Figure S7: Powder EPR spectrum of complex **2a** measured at 4, 15, 50 and 293 K

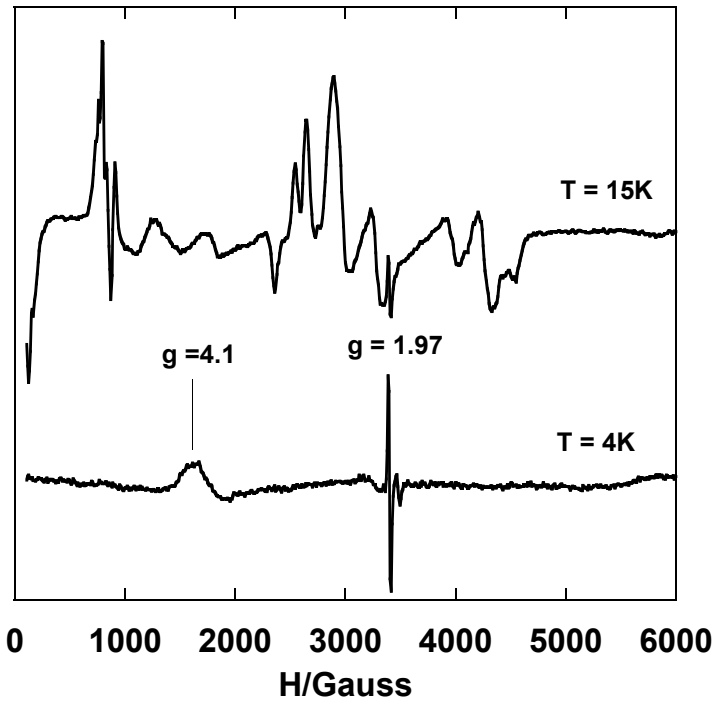

Figure S8: Frozen solution EPR spectrum of **2a** measured at 4, 15 K in $CHCl_3$.

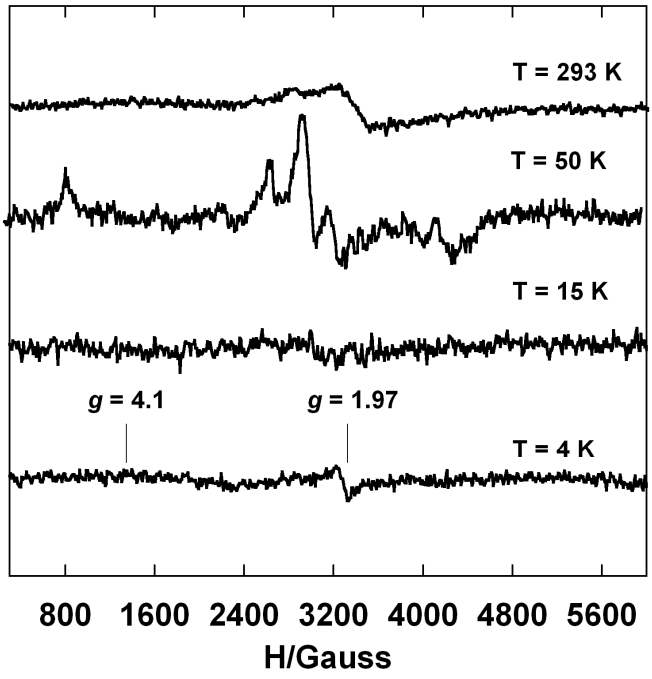

Figure S9: Frozen solution EPR spectrum of **2b** measured at 4, 15, 50, 293 K in $CHCl_3$

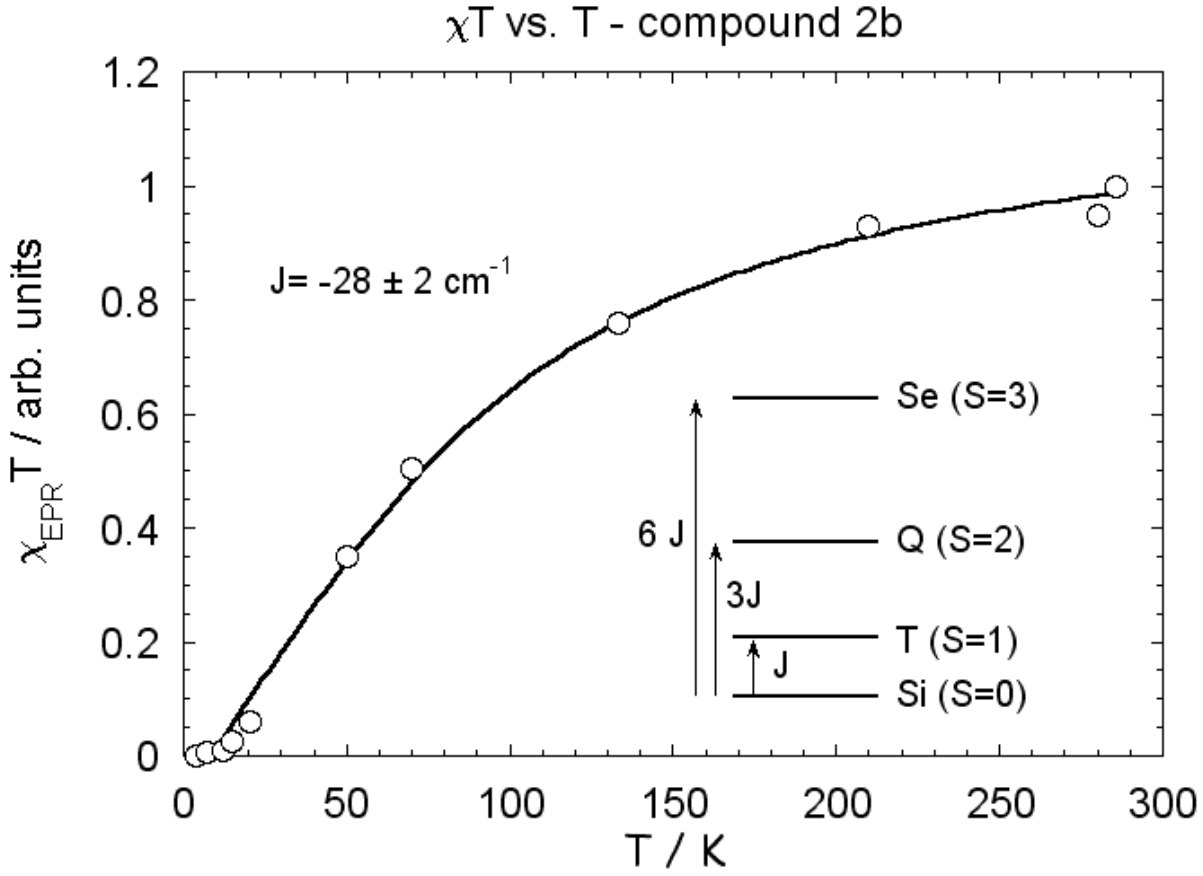

Figure S10. Temperature dependence of the integrated EPR susceptibility for compound **2b**.

The continuous line is the fit to the theoretical expression of the spin susceptibility as explained in the literature.[1] The energy scheme of the resulting spin multiplets distribution is given. The singlet-triplet splitting is equal to J=-28 cm^{-1}, as deduced from SQUID susceptibility (see main text).

[1] (a) Kambe, K., *J. Phys. Soc. Jpn* 1950**, 5,** 48-51 **; (b)** Thompson, M.; Connick, R. E. *Inorg. Chem.* 1981**, 20,** 2279-2285.