Electronic Supplementary Material (ESI) for Dalton Transactions.

Enhancing chalcogen bonding by metal coordination.

Rosa M. Gomila,[a] Antonio Bauzá,[a] and Antonio Frontera[a,*]

[a]Department of Chemistry, Universitat de les Illes Balears
Crta. de Valldemossa km 7.5, 07122 Palma de Mallorca (Spain)
E-mail: toni.frontera@uib.es

Results from the CSD search

Table S1. List of X-ray structures exhibiting metal enhanced-Ch bonds including the CSD code, the ChB donor and acceptor atoms, the Ch···X distance (d, in Å) and the Y–C···X angle (∠, in°).

CSD code	ChB donor	ChB acceptor	d	∠
HEPXEG	Te	Cl	3.249	174.5
ZEYXIN	Te	Cl	3.309	166.8
OGOXAM	Se	Cl	3.341	174.3
XUFHEM	Se	O	3.353	160.8
ZOWYEP	Te	C	3.581	166.8
BEJWUL	Se	Cl	3.376	168.0
OLURIZ	Te	Cl	3.382	167.6
QATVAK	Te	Cl	3.397	162.8
QADDUU	Te Te	Cl Cl	3.401 3.494	174.7
ROXFOB	Te	Cl	3.404	170.9
WICDOD	Se	Cl	3.405	162.4
XILFEE	Se	Cl	3.410	164.7
XUFHIQ	Se	O	3.418	158.9
ZOWYEP10	Te	C	3.583	169.5
QAXKIJ	Te	Cl	3.425	170.3
KEXSAK	Te	Cl	3.429	170.9
XOYTOW	Se	Cl	3.431	167.7
PUYWUC	Se	Cl	3.444	167.8
TOQPEV	Se	C	3.450	157.0
RUHFIM	Te	Cl	3.451	171.1
TAFWIJ	Se	Cl	3.463	176.1
OLUREV	Te	Cl	3.464	166.5
WIXSEB	Te	C	3.465	172.5
DISVIL	Se	Cl	3.470	159.5
UCAJAM	Se	Cl	3.480	160.4

EPULIM	Se	Cl	3.482	161.5
CIPKEU	Se	C	3.484	173.8
KEBXAR	Se	Cl	3.484	164.6
WAVTIY	Se	Cl	3.485	167.0
DEVGUH	S Te	Cl Cl	3.488 3.401	167.1
XIJHIJ	Te	Cl Br	3.509 3.844	174.2
BEJWIZ	Se	C	3.536	168.6
HIXCEX	Te	Cl	3.539	172.9
WIVZAD	Te	Cl	3.551	167.7
TOTRUR	Te	Cl	3.568	173.8
KEBXEV	Se	Cl	3.575	160.6
ZATMEM	Se	Cl	3.579	176.7
ABOREP	Te	Pt	3.585	173.0
TAPYEO	Te	Cl	3.585	154.7
EKIROG	Se	Cl	3.589	165.0
MULZIC	Se	Cl	3.592	174.6
GOYSIZ	Se	Cl	3.618	152.7
CODTEX	Te	Cl	3.621	154.1
JAGZIA	Te	Br	3.647	152.3
COKFIT	Se	C	3.658	176.2
SIDDAL	Te	C	3.666	166.8
VUGWOK	Se	Pd	3.678	150.7[a]
PUYXAJ	Se	Cl	3.679	166.7
NEDTAS	Se	Cl	3.681	160.8
QETFED	Se	Pt	3.697	173.6
MELJUJ	Se	Pd	3.701	175.7
SETFON	Se	Cl	3.701	163.8
CODTAT	Te	Cl	3.706	151.3
QETFAZ	Se	Pd	3.708	170.6
CUHMAV	Te	Pt	3.715	166.5
QADDOO	Te	Cl	3.734	175.8
DIZWAL	Te	Cl	3.753	172.3
DISWAE	Se	Cl	3.760	157.7
KICSIA	Se Se	Br Cl	3.787 3.647	169.6
EKIQUL	Se	Cl	3.795	168.9
PDSECL	Se	Cl	3.820	153.1
LEQSIK	Se	Cl	3.833	166.0
FELPOD	Se	Cl	3.836	159.4
CUHMEZ	Te	Cl	3.850	171.6
YIZPOM	Te	Cl	3.852	153.7
JOZXOL	Te	I	3.862	169.2
BIGDAX	Te	Cl	3.887	160.5
DUWMEN	Se	O	3.909	172.4
CUHMOJ	Te	I	3.937	161.1
REXBOL	Te	Cl	3.937	152.0
WACNIX	Te	Cl	3.989	172.8
UZACEE	Se	I	4.033	165.8

[a]Angle measured to the Cl–Pd bond centroid.

Comparison of ChB geometric parameters between optimized and non-optimized X-ray structures.

Table S2. List of the geometric parameters (d, (in Å) and (C–Ch···X angle, (∠, in °)) regarding the ChBs established in JOXZOL dimer. Opt. stands for optimized structure at the PBE0-D3/def2-TZVP level of theory.

CSD code	ChB donor	ChB acceptor	d	∠
JOXZOL (X-ray)	Te	I	3.679/3.862	173.3/169.2
JOXZOL (Opt.)	Te	I	3.727/3.732	171.4/171.5

Additional information regarding the selected X-ray structures

JOXZOL

This structure corresponds to the *trans*-di-iodo-bis(methyl-phenyl-tellurido)-platinum(II), which exhibits a solid state architecture composed by discrete square-planar *trans* molecules, where the methyl phenyl telluride ligands with the stereochemically active lone pair adopt the RR (and SS) configuration. The authors observed a preference for the *trans* conformation, which was originally attributed to the use of heavy halogens (I) as coligands.

PUYWUC

This structure corresponds to a selenoether functionalized tertiary phosphine. In the original work, the authors remarked the variation of the dihedral angle between the phenyl/phenylene rings attached to Se owing to its potential interaction with the Pt metal center, resulting in weak intermolecular Se···Pt interactions. Also, the authors were intrigued about possible attractive interactions between the Se and Cl atoms belonging to two neighboring units, stating that their interatomic distance was significantly shorter than the sum of their van der Waals radii.

ROXFOB

This structure crystallized in a distorted square planar geometry around a Pd metal center, thus forming a five membered chelate ring. The authors highlighted the contribution of the Cl···H(aromatic), Cl···H (–OCH_3) and Cl···Te interactions in the formation of a three dimensional network.

Cartesian coordinates of complexes 1 to 8

1

C	0.3352470	-1.3458533	-0.5623259
C	0.1691118	-0.6817133	0.6467251
C	-0.1691118	0.6817133	0.6467251

C	-0.3352470	1.3458533	-0.5623259
C	-0.1685559	0.6708619	-1.7662357
C	0.1685559	-0.6708619	-1.7662357
H	0.5850955	-2.3997799	-0.5564025
H	-0.5850955	2.3997799	-0.5564025
H	-0.2981141	1.2016364	-2.7022305
H	0.2981141	-1.2016364	-2.7022305
Se	-0.4739766	1.6529463	2.2565979
Se	0.4739766	-1.6529463	2.2565979
F	1.2173527	1.9125354	2.6838715
F	-1.2173527	-1.9125354	2.6838715

2

C	0.3569074	-1.3396738	-0.6122117
C	0.1794580	-0.6787384	0.5990280
C	-0.1794580	0.6787384	0.5990280
C	-0.3569074	1.3396738	-0.6122117
C	-0.1794243	0.6678118	-1.8165692
C	0.1794243	-0.6678118	-1.8165692
H	0.6223006	-2.3901538	-0.6150726
H	-0.6223006	2.3901538	-0.6150726
H	-0.3178894	1.1967839	-2.7524273
H	0.3178894	-1.1967839	-2.7524273
Te	-0.5285886	1.7497482	2.3775901
Te	0.5285886	-1.7497482	2.3775901
F	1.3252088	1.9657173	2.8196626
F	-1.3252088	-1.9657173	2.8196626

3

C	0.2568538	-1.3691376	-1.3619290
C	0.1306025	-0.6841230	-0.1611536
C	-0.1306025	0.6841230	-0.1611536
C	-0.2568538	1.3691376	-1.3619290
C	-0.1296334	0.6813115	-2.5604096
C	0.1296334	-0.6813115	-2.5604096
H	0.4560144	-2.4346372	-1.3614488
H	-0.4560144	2.4346372	-1.3614488
H	-0.2298395	1.2151708	-3.4977696
H	0.2298395	-1.2151708	-3.4977696
Se	-0.3352239	1.6699106	1.4761313
Se	0.3352239	-1.6699106	1.4761313
F	-2.0776291	1.7810497	1.3554551
F	2.0776291	-1.7810497	1.3554551
Pd	0.0000000	0.0000000	3.0645695
Cl	-0.3512068	1.6838620	4.5788395
Cl	0.3512068	-1.6838620	4.5788395

4

C	0.2421280	-1.3679237	-1.4258950
C	0.1254471	-0.6871495	-0.2184054
C	-0.1254471	0.6871495	-0.2184054

C	-0.2421280	1.3679237	-1.4258950
C	-0.1219873	0.6821612	-2.6267329
C	0.1219873	-0.6821612	-2.6267329
H	0.4294908	-2.4363211	-1.4378664
H	-0.4294908	2.4363211	-1.4378664
H	-0.2154762	1.2181585	-3.5637760
H	0.2154762	-1.2181585	-3.5637760
Te	-0.3333120	1.7981982	1.5844419
Te	0.3333120	-1.7981982	1.5844419
F	-2.2268220	1.8327826	1.4360945
F	2.2268220	-1.8327826	1.4360945
Pd	0.0000000	0.0000000	3.2171071
Cl	-0.3716345	1.8144011	4.6435856
Cl	0.3716345	-1.8144011	4.6435856

5

C	0.0934443	-1.3802742	-1.0951687
C	0.0428087	-0.6982659	0.1173130
C	-0.0428087	0.6982659	0.1173130
C	-0.0934443	1.3802742	-1.0951687
C	-0.0533179	0.6910673	-2.2960387
C	0.0533179	-0.6910673	-2.2960387
H	0.1611119	-2.4614155	-1.0902098
H	-0.1611119	2.4614155	-1.0902098
H	-0.0938848	1.2377812	-3.2308704
H	0.0938848	-1.2377812	-3.2308704
Se	-0.1823626	1.7684258	1.7012359
Se	0.1823626	-1.7684258	1.7012359
F	-1.8497968	2.2899919	1.3358555
F	1.8497968	-2.2899919	1.3358555
C	-2.3129151	-0.8542774	2.1420072
C	2.3129151	0.8542774	2.1420072
O	-3.3448077	-0.5112638	2.4158759
O	3.3448077	0.5112638	2.4158759

6

C	-0.1551862	-1.3651176	-0.7433965
C	-0.0903483	-0.6990356	0.4859998
C	0.0903483	0.6990356	0.4859998
C	0.1551862	1.3651176	-0.7433965
C	0.0674384	0.6912891	-1.9452769
C	-0.0674384	-0.6912891	-1.9452769
H	-0.2634095	-2.4433510	-0.7317532
H	0.2634095	2.4433510	-0.7317532
H	0.1211819	1.2480656	-2.8761978
H	-0.1211819	-1.2480656	-2.8761978
Se	0.2985172	1.8441051	2.0214551
Se	-0.2985172	-1.8441051	2.0214551
F	1.3520241	0.6633562	2.9404830
F	-1.3520241	-0.6633562	2.9404830
Br	-1.1870382	4.1613725	0.8486866

Br	1.1870382	-4.1613725	0.8486866

7

C	0.0111929	-1.3918109	-1.6903005
C	0.0052210	-0.6951987	-0.4903181
C	-0.0052210	0.6951987	-0.4903181
C	-0.0111929	1.3918109	-1.6903005
C	-0.0083373	0.6933082	-2.8892785
C	0.0083373	-0.6933082	-2.8892785
H	0.0181845	-2.4756967	-1.6888214
H	-0.0181845	2.4756967	-1.6888214
H	-0.0143693	1.2371087	-3.8262274
H	0.0143693	-1.2371087	-3.8262274
Se	-0.0500996	1.7061906	1.1472834
Se	0.0500996	-1.7061906	1.1472834
F	-1.7723429	2.0427674	1.0166610
F	1.7723429	-2.0427674	1.0166610
Pd	0.0000000	-0.0000000	2.7509775
Cl	-0.0090455	1.7249409	4.2639749
Cl	0.0090455	-1.7249409	4.2639749
C	-2.7885974	-1.0674824	1.2547823
C	2.7885974	1.0674824	1.2547823
O	-3.8335927	-0.7689184	1.5267554
O	3.8335927	0.7689184	1.5267554

8

C	0.1885676	-1.3726217	-1.5045605
C	0.0919593	-0.6858150	-0.3006753
C	-0.0919593	0.6858150	-0.3006753
C	-0.1885676	1.3726217	-1.5045605
C	-0.0955837	0.6885881	-2.7040069
C	0.0955837	-0.6885881	-2.7040069
H	0.3209286	-2.4484223	-1.4910202
H	-0.3209286	2.4484223	-1.4910202
H	-0.1697325	1.2302998	-3.6416841
H	0.1697325	-1.2302998	-3.6416841
Se	-0.2945205	1.6831064	1.3392605
Se	0.2945205	-1.6831064	1.3392605
F	-2.1406591	1.4888106	1.1688845
F	2.1406591	-1.4888106	1.1688845
Pd	0.0000000	0.0000000	2.9900353
Cl	-0.3144785	1.6934062	4.5802391
Cl	0.3144785	-1.6934062	4.5802391
Br	-2.3265786	-2.2498923	1.0585454
Br	2.3265786	2.2498923	1.0585454

Cartesian coordinates of JOZXOL (Optimized dimer)

Pt	-1.0550482	-1.2428088	0.0243163
I	-2.3349546	-0.3396908	-2.0899117
I	0.0374256	-2.3577805	2.1425128

Te	-2.8764587	0.0861165	1.3036416
Te	0.5482103	-2.8235066	-1.2584945
C	-4.3917530	-1.3820722	1.0677798
C	-4.1075878	-2.7213889	1.3091415
C	-5.0994516	-3.6743070	1.1375936
C	-6.3668779	-3.2958716	0.7145282
C	-6.6440060	-1.9605417	0.4655813
C	-5.6569619	-0.9996097	0.6439728
C	-2.6525221	-0.3137985	3.3844221
C	-0.6385724	-4.5714069	-1.0501824
C	-0.0265809	-5.7780120	-0.7386759
C	-0.7960843	-6.9259387	-0.5990915
C	-2.1701879	-6.8663820	-0.7739981
C	-2.7786558	-5.6571610	-1.0839506
C	-2.0172425	-4.5063609	-1.2177866
C	0.1170931	-2.6555959	-3.3387945
H	-3.1102734	-3.0258610	1.6084691
H	-4.8736167	-4.7180256	1.3253374
H	-7.1385189	-4.0445263	0.5751615
H	-7.6303558	-1.6616667	0.1293636
H	-5.8766714	0.0429393	0.4418609
H	-1.7156345	0.1398063	3.6999586
H	-2.6269365	-1.3895802	3.5370640
H	-3.5011359	0.1400798	3.8944086
H	1.0473590	-5.8285539	-0.5962882
H	-0.3178179	-7.8668770	-0.3518412
H	-2.7695081	-7.7631799	-0.6653056
H	-3.8535840	-5.6024546	-1.2141301
H	-2.4992785	-3.5589053	-1.4342775
H	0.4206371	-1.6593326	-3.6522682
H	-0.9501459	-2.7963965	-3.4885185
H	0.6952336	-3.4230946	-3.8515986
Pt	1.0550482	1.2428088	0.0243163
I	2.3349546	0.3396908	-2.0899117
I	-0.0374256	2.3577805	2.1425128
Te	2.8764587	-0.0861165	1.3036416
Te	-0.5482103	2.8235066	-1.2584945
C	4.3917530	1.3820722	1.0677798
C	4.1075878	2.7213889	1.3091415
C	5.0994516	3.6743070	1.1375936
C	6.3668779	3.2958716	0.7145282
C	6.6440060	1.9605417	0.4655813
C	5.6569619	0.9996097	0.6439728
C	2.6525221	0.3137985	3.3844221
C	0.6385724	4.5714069	-1.0501824
C	0.0265809	5.7780120	-0.7386759
C	0.7960843	6.9259387	-0.5990915
C	2.1701879	6.8663820	-0.7739981
C	2.7786558	5.6571610	-1.0839506
C	2.0172425	4.5063609	-1.2177866
C	-0.1170931	2.6555959	-3.3387945

H	3.1102734	3.0258610	1.6084691
H	4.8736167	4.7180256	1.3253374
H	7.1385189	4.0445263	0.5751615
H	7.6303558	1.6616667	0.1293636
H	5.8766714	-0.0429393	0.4418609
H	1.7156345	-0.1398063	3.6999586
H	2.6269365	1.3895802	3.5370640
H	3.5011359	-0.1400798	3.8944086
H	-1.0473590	5.8285539	-0.5962882
H	0.3178179	7.8668770	-0.3518412
H	2.7695081	7.7631799	-0.6653056
H	3.8535840	5.6024546	-1.2141301
H	2.4992785	3.5589053	-1.4342775
H	-0.4206371	1.6593326	-3.6522682
H	0.9501459	2.7963965	-3.4885185
H	-0.6952336	3.4230946	-3.8515986