X-ray crystal structure determination

The single-crystal X-ray diffraction data for **2**, **6** and **7** were collected on a three-circle Bruker D8 Venture diffractometer (T = 100 K, graphite monochromator, ω and φ scanning mode). The data were indexed and integrated using the *SAINT* program [1], and then scaled and corrected for absorption using the *SADABS* program [2]. The single-crystal X-ray diffraction data for **8**-**11** were collected on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (T = 100 K, graphite monochromator, shutterless ω-scan mode). The data were integrated and corrected for absorption by the *CrysAlisPro* program [3]. For details, see Table S1.

The structures were determined by direct methods and refined by full-matrix least squares technique on F^2 with anisotropic displacement parameters for non-hydrogen atoms. In the crystal of **9**, a solvate acetonitrile molecule was revealed. All attempts to model and refine position of the solvate molecule were unsuccessful. Therefore, its contribution to the total scattering pattern was removed by use of the utility SQUEEZE in PLATON06 [4]. The hydrogen atoms were placed in calculated positions and refined within riding model with fixed isotropic displacement parameters [U_{iso}(H) = 1.5U_{eq}(O), 1.5U_{eq}(C) for the CH_3-groups and 1.2U_{eq}(C) for the other groups]. All calculations were carried out using the SHELXTL program [5].

Crystallographic data for all investigated compounds have been deposited with the Cambridge Crystallographic Data Center, CCDC 2224565 (**2 • H_2O**), CCDC 2224566 (**6**), CCDC 2224567 (**7**), CCDC 2224568 (**8**), CCDC 2224569 (**9**), CCDC 2224570 (**10**) and CCDC 2224571 (**11**). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

References

[1] Bruker, *SAINT*, *v. 8.40A*, Bruker AXS Inc., Madison, WI, **2019**.

[2] L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *J. Appl. Cryst.* **2015**, *48*, 3-10.

[3] Rigaku, *CrysAlisPro Software System, v. 1.171.41.106a*, Rigaku Oxford Diffraction, **2021**.

[4] A. L. Spek, *PLATON*, A Multipurpose Crystallographic Tool, Utrecht University, the Netherlands, **2015**.

[5] G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3-8.

Table S1. Crystal data and structure refinement for all compounds studied.

Identification code	**2 • H_2O**	**6**	**7**	**8**
Empirical formula	$C_9H_{11}ClN_2OSe$	$C_{33}H_{31}BN_2Se$	$C_{33}H_{29}BN_2Se$	$C_{37}H_{31}BN_2Se$
Formula weight	277.61	545.37	543.35	593.41
Crystal size, mm	0.07×0.20×0.20	0.02×0.15×0.70	0.10×0.15×0.20	0.03×0.21×0.23
Radiation, Å	0.71073	0.71073	0.71073	1.54184
Crystal system	Triclinic	Monoclinic	Triclinic	Orthorhombic
Space group	*P*-1	$P2_1/n$	*P*-1	*P*bca
a, Å	7.210(10)	8.848(14)	16.275(4)	12.98660(13)
b, Å	7.496(8)	15.274(13)	20.021(4)	13.29822(14)
c, Å	11.071(18)	20.76(2)	20.459(4)	34.5956(4)
α, deg.	71.93(4)	90	119.240(7)	90
β, deg.	72.88(5)	99.30(6)	100.623(9)	90
γ, deg.	62.68(3)	90	99.813(10)	90
V, $Å^3$	497.2(12)	2769(6)	5447(2)	5974.61(11)
Z	2	4	8	8
Density (calc.), Mg/m^3	1.854	1.308	1.325	1.319
μ, mm^{-1}	4.011	1.380	1.403	1.906
F(000)	276	1128	2240	2448
Theta range, deg.	1.97 – 30.21	1.99 – 26.00	1.34 – 25.00	2.55 – 77.78
Index ranges	$-8 \le h \le 10$, $-10 \le k \le 10$, $-15 \le l \le 15$	$-10 \le h \le 10$, $-18 \le k \le 16$, $-25 \le l \le 24$	$-19 \le h \le 19$, $-23 \le k \le 21$, $-24 \le l \le 24$	$-14 \le h \le 16$, $-16 \le k \le 16$, $-43 \le l \le 43$
Reflections collected	4832	13123	39999	48130
Independent reflections, R_{int}	2842, 0.0275	5408, 0.0507	18949, 0.0418	6307, 0.0436
Reflections observed	2419	3932	14979	5557
R_1 / wR_2 ($I > 2\sigma(I)$)	0.0363 / 0.0859	0.0542 / 0.1217	0.0875 / 0.2322	0.0446 / 0.1191
R_1 / wR_2 (all data)	0.0482 / 0.0910	0.0844 / 0.1333	0.1047 / 0.2403	0.0507 / 0.1236
Goodness-of-fit on F^2	1.023	1.063	1.089	1.059
Extinction coefficient	—	—	—	0.00011(1)
T_{min} / T_{max}	0.504 / 0.746	0.529 / 0.747	0.632 / 0.746	0.506 / 0.939
$\Delta\rho_{max}$ / $\Delta\rho_{min}$, $e \cdot Å^{-3}$	0.678 / -0.911	1.730 / -0.459	2.317 / -0.832	0.917 / -0.586

Table S1 (continued). Crystal data and structure refinement for all compounds studied.

Identification code	**9**	**10 • ½*CH$_3$CN***	**11**
Empirical formula	$C_{41}H_{33}BN_2Se$	$C_{37}H_{29}BCl_2N_2Se$	$C_9H_9AuCl_4N_2Se$
Formula weight	643.46	662.29	562.91
Crystal size, mm	0.11×0.15×0.18	0.02×0.13×0.21	0.21×0.32×0.40
Radiation, Å	1.54184	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$P2_1/c$
a, Å	13.25147(14)	27.692(4)	7.20317(16)
b, Å	36.6506(5)	18.571(2)	11.5792(2)
c, Å	13.08859(16)	24.418(3)	16.7793(4)
α, deg.	90	90	90
β, deg.	91.0491(11)	98.230(4)	95.7281(19)
γ, deg.	90	90	90
V, Å^3	6355.73(13)	12428(3)	1392.52(5)
Z	8	16	4
Density (calc.), Mg/m^3	1.345	1.416	2.685
μ, mm^{-1}	1.837	1.410	13.923
F(000)	2656	5408	1032
Theta range, deg.	2.41 – 83.11	2.19 – 27.00	2.14 – 31.72
Index ranges	$-15 \le h \le 16$, $-46 \le k \le 46$, $-16 \le l \le 16$	$-35 \le h \le 35$, $-23 \le k \le 23$, $-31 \le l \le 31$	$-10 \le h \le 10$, $-15 \le k \le 16$, $-23 \le l \le 22$
Reflections collected	214248	92586	28880
Independent reflections, R_{int}	13562, 0.1024	13373, 0.0993	4120, 0.0873
Reflections observed	12320	7152	3707
R_1 / wR_2 ($I > 2\sigma(I)$)	0.0986 / 0.2227	0.0835 / 0.1661	0.0331 / 0.0801
R_1 / wR_2 (all data)	0.1042 / 0.2263	0.1655 / 0.2012	0.0382 / 0.0824
Goodness-of-fit on F^2	1.011	1.010	1.024
Extinction coefficient	—	0.00061(6)	0.0029(2)
T_{min} / T_{max}	0.548 / 0.817	0.778 / 0.885	0.025 / 0.143
$\Delta\rho_{max}$ / $\Delta\rho_{min}$, e·Å^{-3}	1.456 / -0.764	0.983 / -0.743	3.185 / -2.542