SUPPORTING INFORMATION

Exceptional Structural Compliance of the $B_{12}F_{12}^{2-}$ Superweak Anion

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Abbreviations used in this document: $Y^{2-} = B_{12}F_{12}^{2-}$; ⊙ = B_{12} centroid

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Table S1. Bond valence parameters used in this work for Ag–X distances (X = F, O, N, C, Cl)[a]

cation	R_{AgF}	R_{AgO}	R_{AgN}	R_{AgC}	R_{AgCl}
Ag^{+}	1.80	1.805	1.85	1.85	2.09

[a] The bond valence contribution for each Ag–X distance (i.e., bv(AgX); X = F, O, N, C, and Cl) is calculated using the formula bv(MX) = exp[(R_{AgX} − d_{AgX})/0.37], where d_{AgX} is the Ag–X distance. The R_{AgX} values were taken from Brese, N. E.; O'Keeffe, M. *Acta Cryst.* **1991**, *B47*, 192–197 except for R_{AgC}, which was derived for this work.

Table S2. Ag–X bond distances and bond valences for $Ag_2(CH_3CN)_8(B_{12}F_{12})$ (this work)

Ag2(CH3CN)8(B12F12)	bond	distance	bv param	bv	bv/Σ(bv)
(this work)	Ag-N6A	2.263	1.850	0.328	0.290
	Ag-N2	2.225	1.850	0.363	0.321
	Ag-N1	2.295	1.850	0.300	0.266
	Ag-N3	2.419	1.850	0.215	0.190
	Ag-F	3.351	1.805	0.015	
	Ag-F	3.857	1.805	0.004	
Σ(bv) does not include			Σ(bv) =	1.206	
bv values < 0.03					
			ave. all 4 Ag-N	0.301	0.234
			ave. 3 strongest	0.330	0.253

Table S3. Ag–X bond distances and bond valences for $Ag_2(CH_3CN)_5(B_{12}F_{12})$ (this work)

Ag2(CH3CN)5(B12F12)	bond	distance, A	bv param	bv	bv/Σ(bv)
(this work)	Ag-N2	2.139	1.850	0.458	0.391
	Ag-N3	2.160	1.850	0.433	0.369
	Ag-N1	2.453	1.850	0.196	0.167
	Ag-F1	2.920	1.805	0.049	0.042
	Ag-F2	3.041	1.805	0.035	0.030
			Σ(bv) =	1.171	
			ave. all 3 Ag-N	0.362	0.309
			ave. 2 strongest	0.445	0.380

Table S4. Ag–X bond distances and bond valences for $Ag_2(CH_3CN)_4(B_{12}F_{12})$ (this work)

Ag2(CH3CN)4(B12F12)	bond	distance	bv param	bv	bv/Σ(bv)
(this work)	Ag-N1	2.101	1.850	0.507	0.412
	Ag-N1A	2.101	1.850	0.507	0.412
	Ag-F1	2.797	1.805	0.068	0.056
	Ag-F1A	2.797	1.805	0.068	0.056
	Ag-F4	2.992	1.805	0.040	0.033
	Ag-F4A	2.992	1.805	0.040	0.033
			Σ(bv) =	1.233	

Table S5. Ag–X bond distances and bond valences for $Ag(CH_3CN)_4(SO_3F)$[a]

Ag(CH3CN)4(SO3F)	bond	distance	bv param	bv	bv/Σ(bv)
Dortbudak *ZNaturforschB* **2014**	Ag-N6A	2.248	1.850	0.341	0.270
	Ag-N2	2.270	1.850	0.321	0.255
	Ag-N1	2.281	1.850	0.312	0.247
	Ag-N3	2.313	1.850	0.286	0.227
			Σ(bv) =	1.261	1.000
			ave. all 4 Ag-N	0.315	0.250

[a] Dortbudak et al., *Z. Naturforsch. B.* **2014**, *69*, 373–375 (ref 24 in the main text).

Table S6. Ag–X bond distances and bond valences for $Ag_2(PhCH_3)_6(B_{12}F_{12})$ (this work)

Ag2(PhCH3)6(B12F12)	bond	distance	bv param	bv	bv/Σ(bv)
(this work)	Ag-C	2.408	1.85	0.221	0.234
	Ag-C	2.427	1.85	0.210	0.223
	Ag-C	2.512	1.85	0.167	0.177
	Ag-C	2.600	1.85	0.132	0.140
	Ag-C	2.652	1.85	0.114	0.121
	Ag-C	2.899	1.85	0.059	0.062
	Ag-F	2.991	1.80	0.040	0.042
			Σ(bv) =	0.944	
			ave. all six Ag-C	0.151	0.160
			ave. 4 strongest	0.183	0.194
			ave. 3 strongest	0.200	0.212

Table S7. Ag–X bond distances and bond valences for $Ag(PhCH_3)_3(Li(Al_2F_5(C(SiMe_3)_3)_2)_2)$[a]

Ag(PhCH3)3(X)	bond	distance	bv param	bv	bv/Σ(bv)
Roesky et al. *OM* **1998**	Ag-C	2.396	1.85	0.229	0.240
	Ag-C	2.408	1.85	0.221	0.232
X = Li(Al2F5(C(SiMe3)3)2)2	Ag-C	2.504	1.85	0.171	0.179
	Ag-C	2.544	1.85	0.153	0.161
	Ag-C	2.696	1.85	0.102	0.107
	Ag-C	2.790	1.85	0.079	0.083
			Σ(bv) =	0.954	
			ave. Ag-C bv	0.159	0.167
			ave. 4 strongest	0.193	0.202
			ave. 3 strongest	0.207	0.217

[a] Roesky et al., *Organometallics* **1998**, *17*, 4326–4328 (ref 26 in the main text).

Table S8. Ag–X bond distances and bond valences for $Ag(PhCH_3)_2(Al(HFIP)_4)$[a]

Ag(PhCH3)2(Al(HFIP)4)	bond	distance	bv param	bv	bv/Σ(bv)		bond	distance	bv param	bv	bv/Σ(bv)
Krossing *Chem. Eur. J.* **2001**	Ag1-C	2.363	1.850	0.250	0.266		Ag2-C	2.416	1.850	0.217	0.221
	Ag1-C	2.435	1.850	0.206	0.219		Ag2-C	2.469	1.850	0.188	0.191
HFIP = OCH(CF3)2	Ag1-C	2.593	1.850	0.134	0.143		Ag2-C	2.484	1.850	0.180	0.184
	Ag1-C	2.647	1.850	0.116	0.123		Ag2-C	2.496	1.850	0.174	0.178
	Ag1-O	2.596	1.805	0.118	0.125		Ag2-O	2.541	1.805	0.137	0.139
	Ag1-O	2.599	1.805	0.117	0.124		Ag2-O	2.715	1.805	0.085	0.087
Σ(bv) does not include	Ag1-F	3.374	1.800	0.014			Ag2-F	3.397	1.800	0.013	
bv values < 0.03	Ag1-F	3.482	1.800	0.011			Ag2-F	3.505	1.800	0.010	
			Σ(bv) =	0.941					Σ(bv) =	0.981	
			ave. all 4 Ag-C	0.176	0.187				ave. all 4 Ag-C	0.190	0.194
			ave. 2 strongest	0.228	0.242				ave. 2 strongest	0.202	0.206

[a] Krossing, *Chem. Eur. J.* **2001**, *7*, 490–502 (ref 27 in the main text).

Table S9. Ag–X bond distances and bond valences for $Ag(H_3O)_4(B_{12}F_{12})$[a]

Ag2(H2O)4(B12F12)	bond	distance	bv param	bv	bv/Σ(bv)		bond	distance	bv param	bv	bv/Σ(bv)
Malischewski *Inorg. Chem.* **2016**	Ag1-O1	2.371	1.805	0.217	0.250		Ag2-O2	2.376	1.805	0.214	0.240
	Ag1-O3	2.408	1.805	0.196	0.226		Ag2-O4	2.388	1.805	0.207	0.232
	Ag1-O2	2.411	1.805	0.194	0.224		Ag2-O3	2.467	1.805	0.167	0.188
	Ag1-O4	2.524	1.805	0.143	0.165		Ag2-O1	2.511	1.805	0.148	0.167
	Ag1-F8	2.734	1.800	0.080	0.092		Ag2-F11	2.742	1.800	0.078	0.088
	Ag1-F11	3.021	1.800	0.037	0.043		Ag2-F12	2.751	1.800	0.077	0.086
			Σ(bv) =	0.867					Σ(bv) =	0.891	
			ave. all 4 Ag-OH2	0.188					ave. all 4 Ag-OH2	0.184	

[a] Malischewski et al., *Inorg. Chem.* **2016**, in press (doi 10.1021/om9803016; ref 1 in the main text).

Table S10. Ag–X bond distances and bond valences for $Ag(SO_2)_6(B_{12}F_{12})$[a]

Ag2(SO2)6(B12F12)	bond	distance	bv param	bv	bv/Σ(bv)
Malischewski *Inorg. Chem.* **2016**	Ag-O6	2.566	1.805	0.128	0.137
	Ag-O4	2.564	1.805	0.129	0.138
	Ag-O2	2.525	1.805	0.143	0.153
	Ag-O1A	2.661	1.805	0.099	0.106
	Ag-O3A	2.658	1.805	0.100	0.107
	Ag-O5A	2.790	1.805	0.070	0.075
	Ag-F1A	2.558	1.800	0.129	0.138
	Ag-F4	2.541	1.800	0.135	0.145
			Σ(bv) =	0.932	
			ave .all 6 Ag-OSO	0.111	0.119

[a] Malischewski et al., *Inorg. Chem.* **2016**, in press (doi 10.1021/om9803016; ref 1 in the main text).

Table S11. Ag–X bond distances and bond valences for $Ag_2(CH_2Cl_2)_4(B_{12}F_{12})$ (this work)

Ag2(CH2Cl2)4(B12F12)	bond	distance	bv param	bv	bv/Σ(bv)
(this work)	Ag-Cl	2.659	2.090	0.215	0.224
	Ag-Cl	2.691	2.090	0.197	0.205
	Ag-Cl	2.834	2.090	0.134	0.139
	Ag-Cl	2.884	2.090	0.117	0.122
	Ag-F	2.634	1.800	0.105	0.109
	Ag-F	2.649	1.800	0.101	0.105
	Ag-F	2.679	1.800	0.093	0.097
			Σ(bv) =	0.962	
			ave. all 4 Ag-Cl	0.166	0.173
			ave. 2 strongest	0.206	0.214

Table S12. Ag–X bond distances and bond valences for $Ag_2(CH_2Cl_2)_4(Pd(OTeF_5)_4)$[a]

Ag2(CH2Cl2)4(Pd(OTeF5)4)	bond	distance	bv param	bv	bv/Σ(bv)
Colsman *J. Am. Chem. Soc.* **1990**	Ag-Cl	2.775	2.090	0.157	0.171
	Ag-Cl	2.811	2.090	0.142	0.156
	Ag-Cl	2.859	2.090	0.125	0.137
	Ag-Cl	2.882	2.090	0.118	0.128
	Ag-O	2.532	1.805	0.140	0.153
	Ag-O	2.404	1.805	0.198	0.216
	Ag-F	3.030	1.800	0.036	0.039
			Σ(bv) =	0.916	
			ave. all 4 Ag-Cl	0.136	0.148
			ave. 2 strongest	0.150	0.164

[a] Colsman et al., *J. Am. Chem. Soc.* **1990**, *112*, 2349–2362 (ref 12 in the main text).

Table S13. Ag–X bond distances and bond valences for $Ag(CH_2Cl_2)_2(SbF_6)$[a]

Ag(CH2Cl2)2(SbF6)	bond	distance	bv param	bv	bv/Σ(bv)
Decken *Chem. Eur. J.* **2009**	Ag-Cl	2.903	2.090	0.111	0.114
	Ag-Cl	2.706	2.090	0.189	0.194
	Ag-Cl	2.657	2.090	0.216	0.222
	Ag-Cl	3.128	2.090	0.060	0.062
	Ag-F	2.601	1.800	0.115	0.118
	Ag-F	2.525	1.800	0.141	0.145
	Ag-F	2.524	1.800	0.141	0.145
			Σ(bv) =	0.974	
			ave. all 4 Ag-Cl	0.144	0.148
			ave. 2 strongest	0.203	0.208

[a] Decken et al., *Chem. Eur. J.* **2009**, *15*, 6504–6517 (ref 31 in the main text).

Table S14. Ag–X bond distances and bond valences for $Ag_2(CH_2Cl_2)_6(Ti(OTeF_5)_6)$[a]

Ag2(CH2Cl2)6(Ti(OTeF5)6)	bond	distance	R	bv	bv/Σ(bv)
van Seggen *Inorg. Chem.* **1995**	Ag-Cl	2.656	2.090	0.217	0.230
	Ag-Cl	2.702	2.090	0.191	0.203
	Ag-Cl	2.719	2.090	0.183	0.194
	Ag-Cl	2.856	2.090	0.126	0.134
	Ag-Cl	3.030	2.090	0.079	0.084
	Ag-Cl	3.049	2.090	0.075	0.079
	Ag-F	3.029	1.800	0.036	0.038
	Ag-F	3.033	1.800	0.036	0.038
			Σ(bv) =	0.942	
			ave. all 6 Ag-Cl	0.145	0.154
			ave. 3 strongest	0.197	0.209

[a] van Seggen et al., *J. Am. Chem. Soc.* **1990**, *112*, 2349–2362 (ref 32 in the main text).

Table S15. Ag–X bond distances and bond valences for $Ag(CH_2Cl_2)(Al(HFTB)_4)$[a]

Ag(CH2Cl2)(Al(HFTB)4)	bond	distance	R	bv	bv/Σ(bv)
Krossing *Chem. Eur. J.* **2001**	Ag-Cl	2.613	2.090	0.243	0.244
	Ag-Cl	2.874	2.090	0.120	0.121
	Ag-F	2.857	1.800	0.057	0.058
	Ag-F	2.931	1.800	0.047	0.047
	Ag-F	2.924	1.800	0.048	0.048
	Ag-F	2.849	1.800	0.059	0.059
	Ag-O	2.377	1.805	0.213	0.214
	Ag-O	2.386	1.805	0.208	0.209
			Σ(bv) =	0.996	
			ave. both Ag-Cl	0.182	0.183

[a] Krossing et al., *Chem. Eur. J.* **2001**, *7*, 490–502 (ref 27 in the main text).

Table S16. Ag–X bond distances and bond valences for $Ag(CH_3CN)_2(B(C_6H_3(CF_3)_2)_4)$[a]

Ag(CH3CN)2(B(C6H3(CF3)2)4	bond	distance	bv param	bv	bv/Σ(bv)
Zhang *New J. Chem.* **2005**	Ag-N	2.097	1.850	0.513	0.416
	Ag-N	2.097	1.850	0.513	0.416
	Ag-F	3.132	1.805	0.028	0.022
	Ag-F	3.132	1.805	0.028	0.022
			Σ(bv) =	1.081	

[a] Zhang et al., *New J. Chem. Eur. J.* **2005**, *29*, 366–370 (ref 25 in the main text). There are two unique $Ag(CH_3CN)_2^+$ cations in the structure. The second cation has two symmetry related Ag–N bonds of 2.066(4) Å and two symmetry related Ag–F bonds of 2.131 Å, giving a Σ(bv) value of 1.171.

Table S17. Ag–X bond distances and bond valences for $Ag(CHPh_3)(1\text{-Me-}CB_{11}F_{12})$[a]

Ag(CHPh3)(1-Me-CB11F11)	bond	distance	bv param	bv	bv/Σ(bv)
Ivanov *Cryst. Growth Design* **2004**	Ag-C	2.550	1.85	0.151	0.149
	Ag-C	2.551	1.85	0.150	0.149
	Ag-C	2.407	1.85	0.222	0.220
	Ag-C	2.468	1.85	0.188	0.186
	Ag-C	2.451	1.85	0.197	0.195
	Ag-C	2.692	1.85	0.103	0.102
			Σ(bv) =	1.011	
			ave. all six Ag-C	0.169	
			ave. 3 strongest	0.202	

[a] Ivanov et al., *Crystal Growth Des.* **2004**, *4*, 249–254 (ref 28 in the main text).

Table S18. Ag–X bond distances and bond valences for $Ag(C_6H_6)_3(B(C_6F_5)_4)$[a]

Ag(C6H6)3(B(C6F5)4)	bond	distance	bv param	bv	bv/Σ(bv)
Ogawa *Organometallics* **2005**	Ag-C	2.391	1.85	0.232	0.231
	Ag-C	2.398	1.85	0.227	0.226
	Ag-C	2.400	1.85	0.226	0.225
	Ag-C	2.646	1.85	0.116	0.116
	Ag-C	2.660	1.85	0.112	0.111
	Ag-C	2.737	1.85	0.091	0.091
			Σ(bv) =	1.005	
			ave. all six Ag-C	0.167	0.160
			ave. 3 strongest	0.228	0.194

[a] Ogawa et al., *Organometallics* **2005**, *24*, 4842–4844 (ref 29 in the main text).

Table S19. Ag–X bond distances and bond valences for $Ag(C_6D_6)_3(BF_4)$[a]

Ag(C6D6)3(BF4)	bond	distance	bv param	bv	bv/Σ(bv)
Batsanov *JOMC* **1998**	Ag-C	2.480	1.85	0.182	0.190
	Ag-C	2.487	1.85	0.179	0.187
	Ag-C	2.525	1.85	0.161	0.169
	Ag-C	2.536	1.85	0.157	0.164
	Ag-C	2.880	1.85	0.062	0.065
	Ag-C	2.889	1.85	0.060	0.063
	Ag-F	2.488	1.80	0.156	0.163
			Σ(bv) =	0.957	
			ave. all six Ag-C	0.134	0.160
			ave. 4 strongest	0.170	0.194

[a] Batsanov et al., *J. Organometal. Chem.* **1998**, *550*, 59–61 (ref 30 in the main text).

Table S20. Ag–X bond distances and bond valences for $Ag(CH_3CN)_4(B(C_6F_5)_4)$[a]

Ag(CH3CN)4(B(C6F5)4)	bond	distance	bv param	bv	bv/Σ(bv)
Zhang *New J. Chem.* **2005**	Ag-N	2.265	1.850	0.326	0.264
	Ag-N	2.279	1.850	0.314	0.254
	Ag-N	2.281	1.850	0.312	0.253
	Ag-N	2.298	1.850	0.298	0.242
			Σ(bv) =	1.249	

[a] Zhang et al., *New J. Chem.* **2005**, *29*, 366–370 (ref 25 in the main text).

Table S21. Ag–X bond distances and bond valences for $Ag(CH_3CN)_4(ClO_4)$[a]

Ag(CH3CN)4(ClO4)	bond	distance	bv param	bv	bv/Σ(bv)
Jones *Z. Krist.* **1993**	Ag-N	2.240	1.850	0.349	0.283
	Ag-N	2.251	1.850	0.338	0.274
	Ag-N	2.247	1.850	0.342	0.277
	Ag-N	2.273	1.850	0.319	0.259
			Σ(bv) =	1.348	

[a] Jones et al., *Z. Krist.* **1993**, *208*, 213–218 (ref 68 in the main text).

Table S22. Ag–X bond distances and bond valences for $Ag(CH_3CN)_4(Co(C_2B_9H_{11})_2)$[a]

Ag(CH3CN)4(Co(C2B9H11)2)	bond	distance	bv param	bv	bv/Σ(bv)
Xie *JOMC* **2000**	Ag-N1	2.31	1.850	0.288	0.229
	Ag-N1'	2.31	1.850	0.288	0.229
	Ag-N2	2.19	1.850	0.399	0.316
	Ag-N2'	2.19	1.850	0.399	0.316
			Σ(bv) =	1.375	1.090
			ave. all 4 Ag-N	0.344	0.250

[a] Xie et al., *J. Organometal.Chem.* **2000**, *613*, 99–104 (ref 69 in the main text).

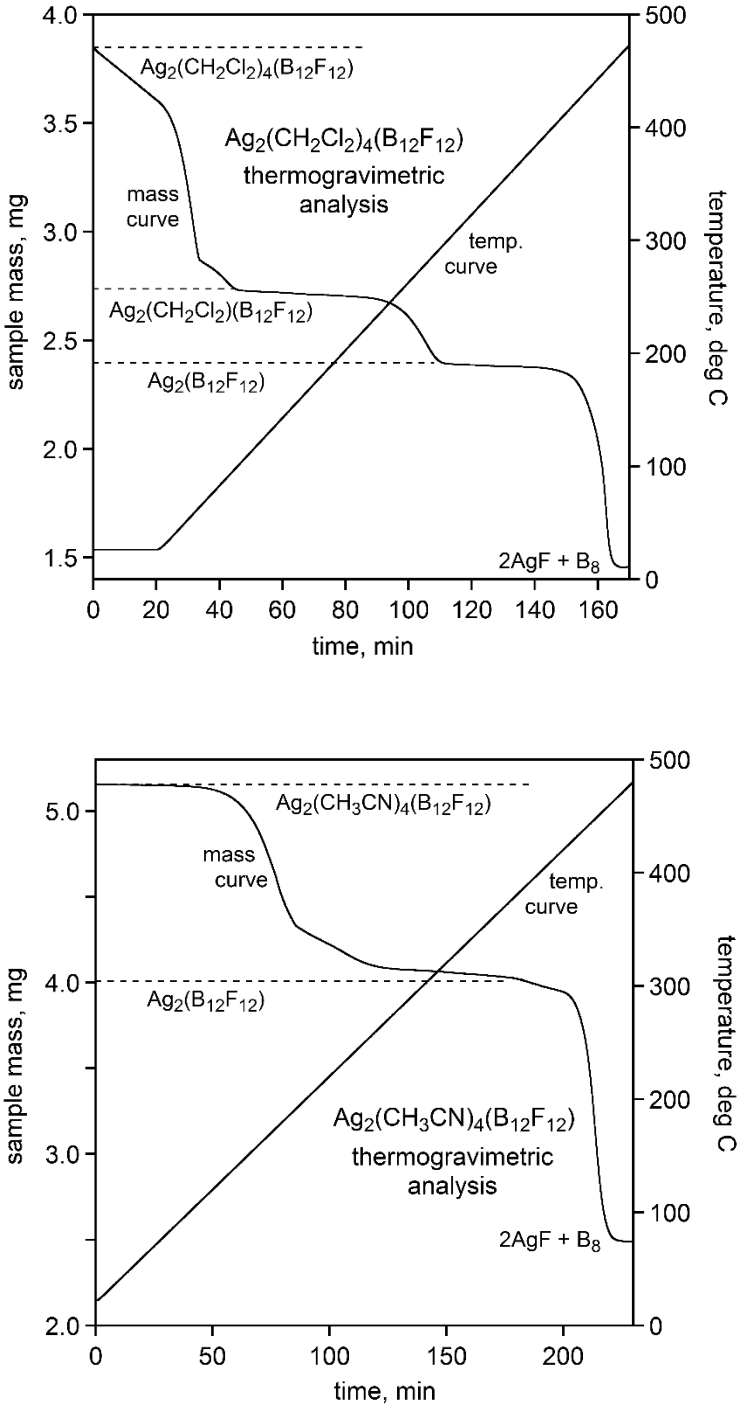

Figure S1. Thermogravimetric plots for $Ag_2(CH_2Cl_2)_4(B_{12}F_{12})$ (top) and $Ag_2(CH_3CN)_4(B_{12}F_{12})$ (bottom). The final mass designated $2AgF + B_8$ is consistant with this composition. However, the chemical nature of the final decomposed product was not investigated experimentally.

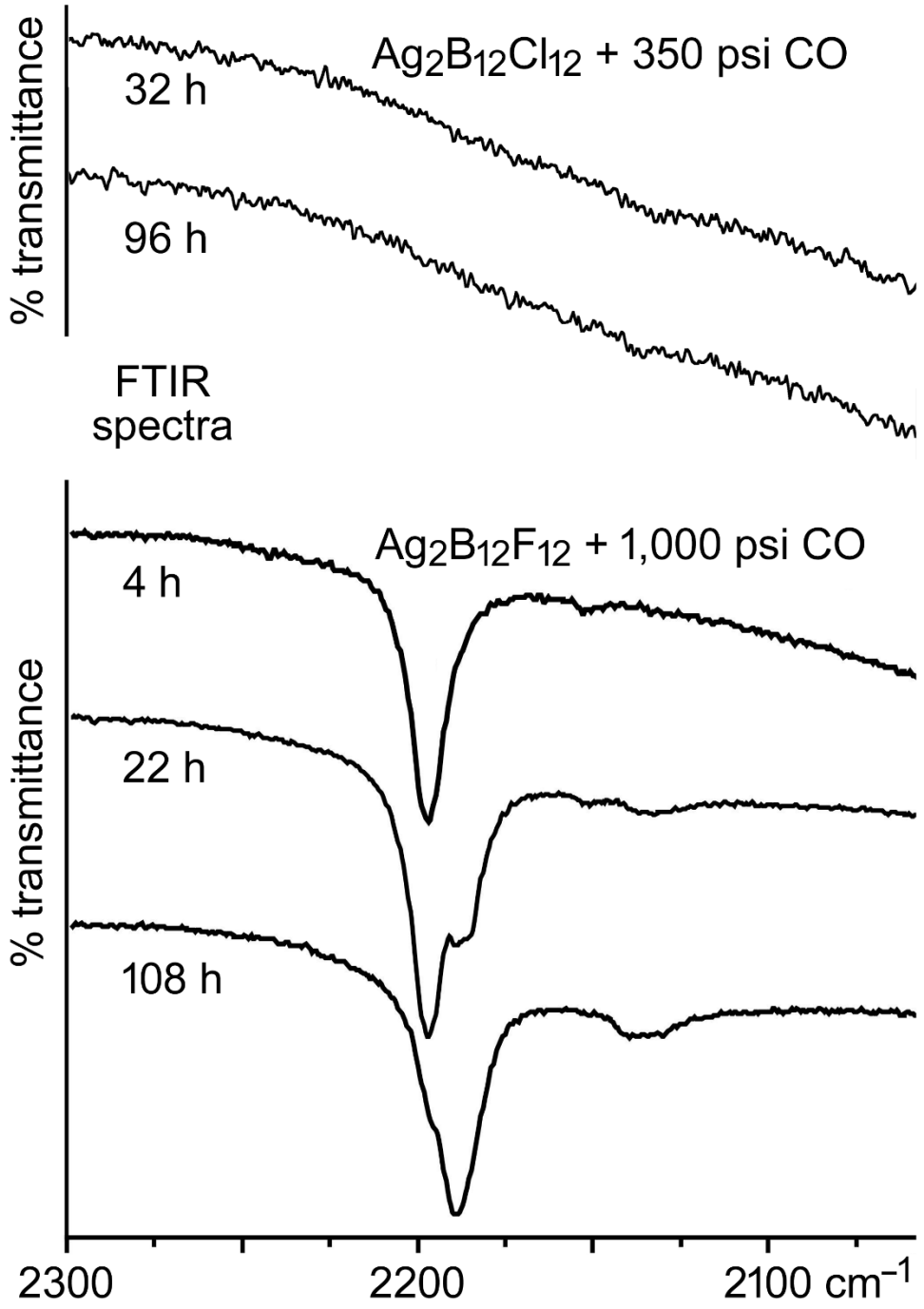

Figure S2. FTIR spectra of Nujol mulls of $Ag_2(B_{12}Cl_{12})$ (top) and $Ag_2(B_{12}F_{12})$ (bottom) under high pressures of CO in a high-pressure transmission IR cell of local design (see text for details). No $Ag(CO)_n^+$ species were observed when the sample was $Ag_2(B_{12}Cl_{12})$.

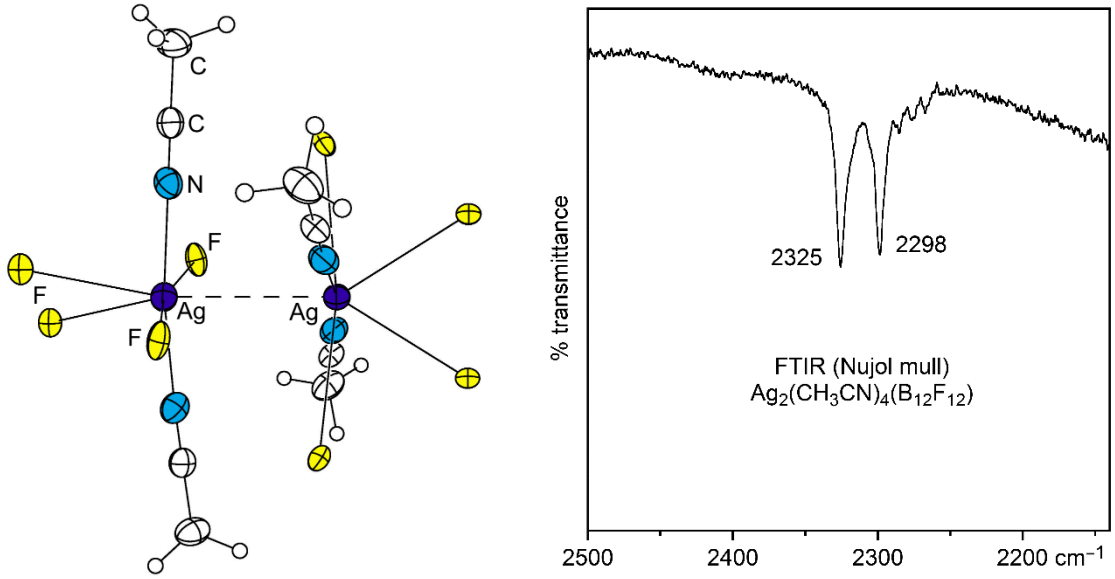

Figure S3. FTIR spectrum of a Nujol mull of $Ag(CH_3CN)_4(B(C_6F_5)_4)$. Isolated linear $Ag(CH_3CN)_2^+$ complexes should give rise to only one IR ν(CN) band. The presence of two bands indicates that the pair of $Ag(CH_3CN)_2^+$ complexes with a Ag···Ag separation of 3.131 Å are acting as a vibrationally-coupled unit, giving rise to two IR ν(CN) bands and presumably two Raman ν(CN) bands. The dihedral angle formed by the two AgN_2 planes is 58.7°.

Table S23. Selected Gas-Phase Bond Dissociation Energies[a]

species	BDE, kJ mol^{-1}	reference (in this PDF)
H_2O–Na^+	100(5)	1
H_2O–K^+	75(4)	1
H_2O–Cu^+	157(8)	2
H_2O–Ag^+	131(8)	3
(C_6H_6)–Na^+	93(6)	4
(C_6H_6)–K^+	73(4)	4
(C_6H_6)–Cu^+	217(6)	5
(C_6H_6)–Ag^+	156(7)	6
$(C_6H_5CH_3)$–K^+	80(5)	7
$(C_6H_5CH_3)$–Cu^+	219(10)	5
(CH_3CN)–Na^+	102(4)	8
(CH_3CN)–K^+	102(4)	8
(CH_3CN)–Cu^+	238(3)	9
(CH_3CN)–Ag^+	162(6)	10
OC–Na^+	31(8)	11
OC–K^+	19(5)	11
OC–Cu^+	149(7)	12
OC–Ag^+	89(5)	12

[a] Most of these values are from threshold collision-induced dissociation experiments and are adjusted for 0 K. See individual references for details.

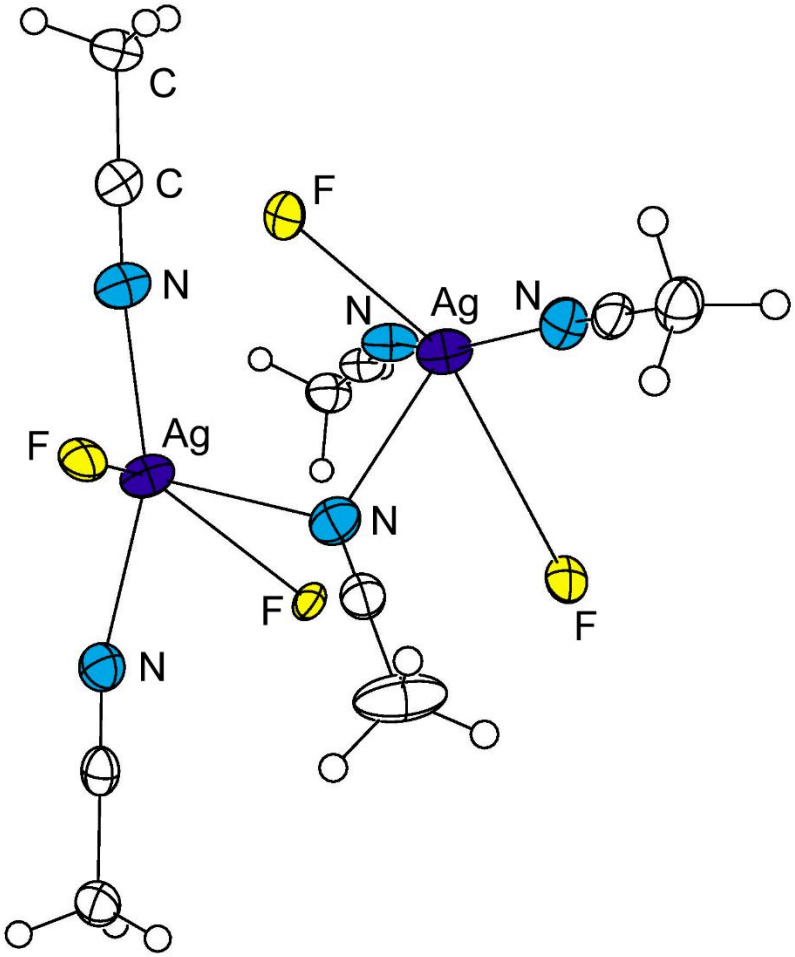

Figure S4. Drawing of the $[(CH_3CN)_2Ag(\mu\text{-}CH_3CN\text{-}\kappa^1,\kappa^2N)Ag(CH_3CN)_2]^{2+}$ dinuclear complex and the four F atoms bonded to it in the structure of $Ag_2(CH_3CN)_5(B_{12}F_{12})$.

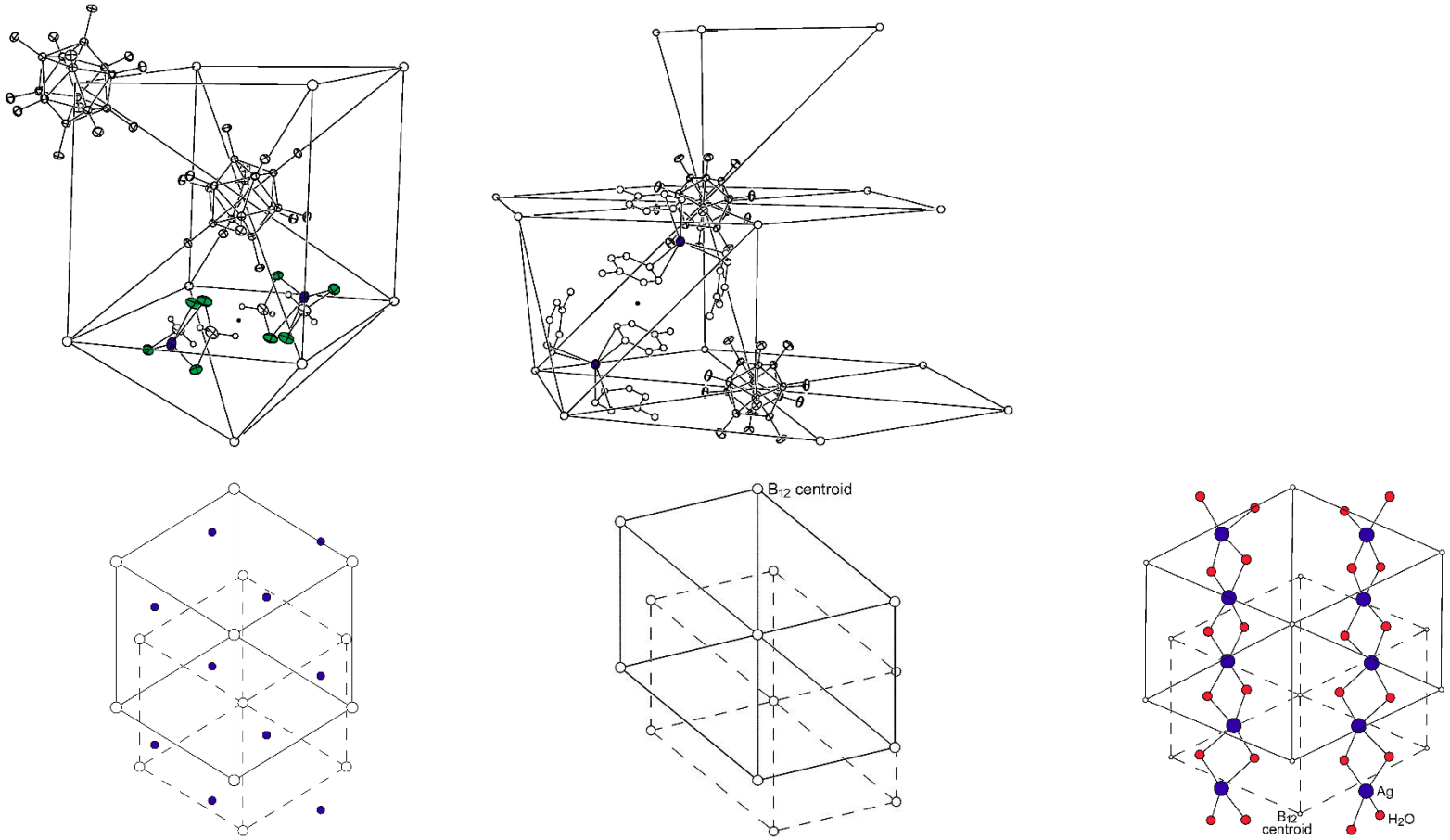

Figure S5. Packing of $Ag(L)_n^+$ cations and $B_{12}F_{12}^{2-}$ anions (Y^{2-}) in the structures of $Ag_2(CH_2Cl_2)_4(Y)$ (left; this work; 50% thermal ellipsoids except for H atoms), $Ag_2(PhCH_3)_6(Y)$ (middle; this work; 50% thermal ellipsoids except for C atoms; H atoms omitted for clarity), and $Ag_2(H_2O)_4(Y)$ (right; ref 13; H atoms omitted for clarity). In all three structures the B_{12} centroids (⊙s) form rigorously-planar, idealized close-packed arrays that are not stacked in a close-packed manner in the third dimension. Instead, they are offset (i) by ca. one-half of the ⊙···⊙ distance along one of their respective ⊙···⊙···⊙ vectors and (ii) by a much smaller displacement perpendicular to the aforementioned ⊙···⊙···⊙ vector.

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