--Supplemental Material--

to:

Extending the Coordination Chemistry of Molecular P_4S_3: The Polymeric $Ag(P_4S_3)^+$ and $Ag(P_4S_3)_2^+$ Cations

by:

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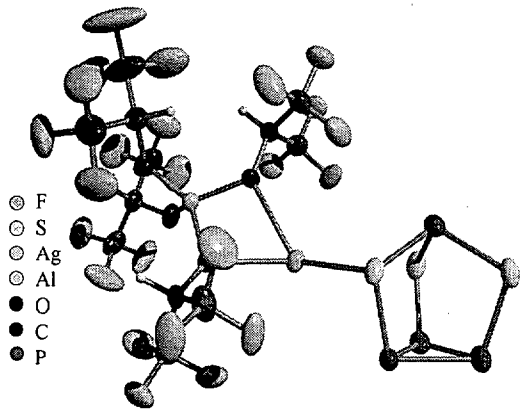
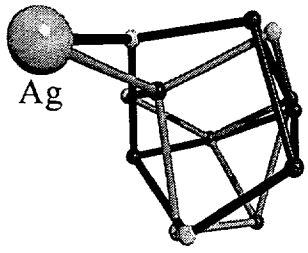
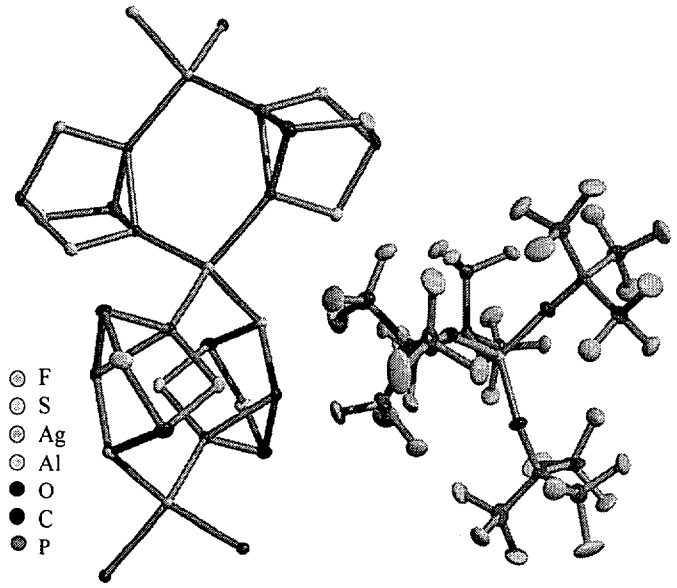
Overall Structure with Anions and Disorder in 1



S-Figure 1: The solid state structure of the asymmetric unit of **1** (68.6 % majority structure shown). Thermal ellipsoids were drawn at the 25 % probability level.



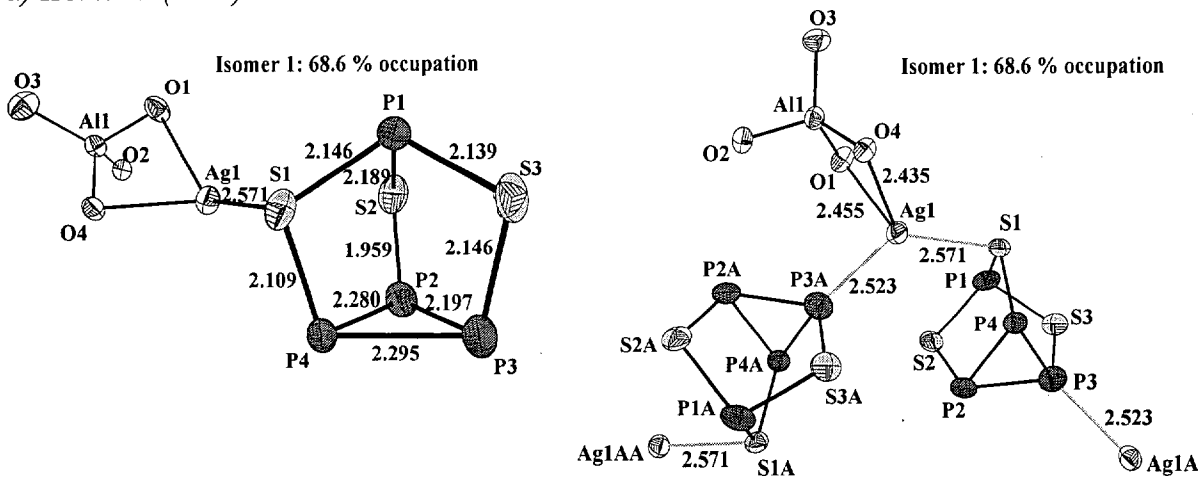
S-Figure 2: Resolved disorder of the coordinated P_4S_3 molecules in **1**. The 68.6% majority fraction adopts the structure shown with black bonds, the 31.4 % minority structure is shown with gray bonds.



S-Figure 3: The solid state structure of **2**. Thermal ellipsoids were drawn at the 25 % probability level. One complete repetitive $[Ag(P_4S_3)_2]_2$ unit of the infinite chain of $[Ag(P_4S_3)_2]_\infty$ is shown. The P and S Atoms completing the coordination of the upper and lower Ag atoms are also shown.

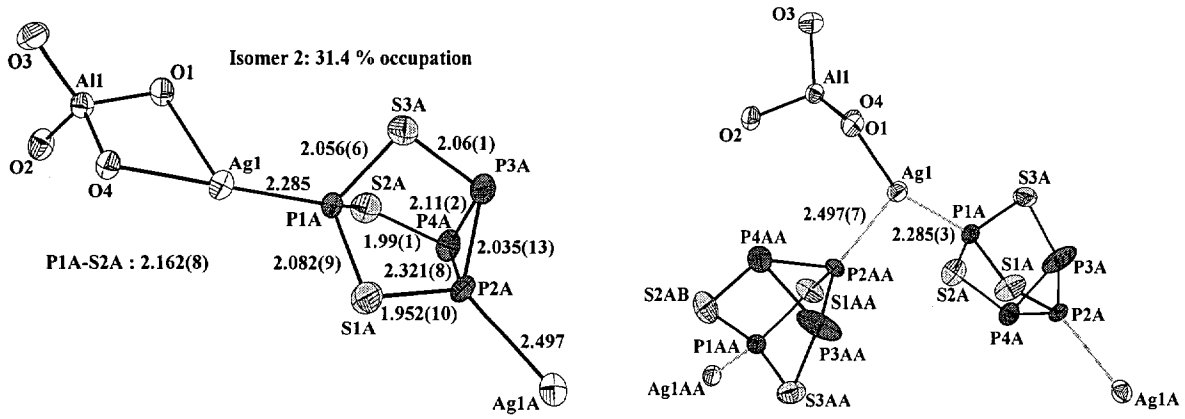
Structural Parameters of 1-2

*a) Isomer 1 (= **1a**)*



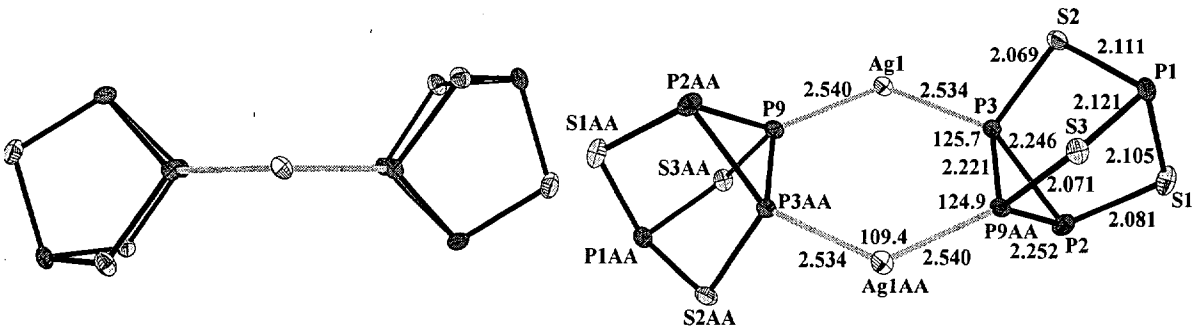
S-Figure 4: Structural parameters of isomer 1 in **1a**. Distances are given in Å, standard deviations are 0.004 to 0.005Å for distances.

*b) Isomer 2 (= **1b**)*



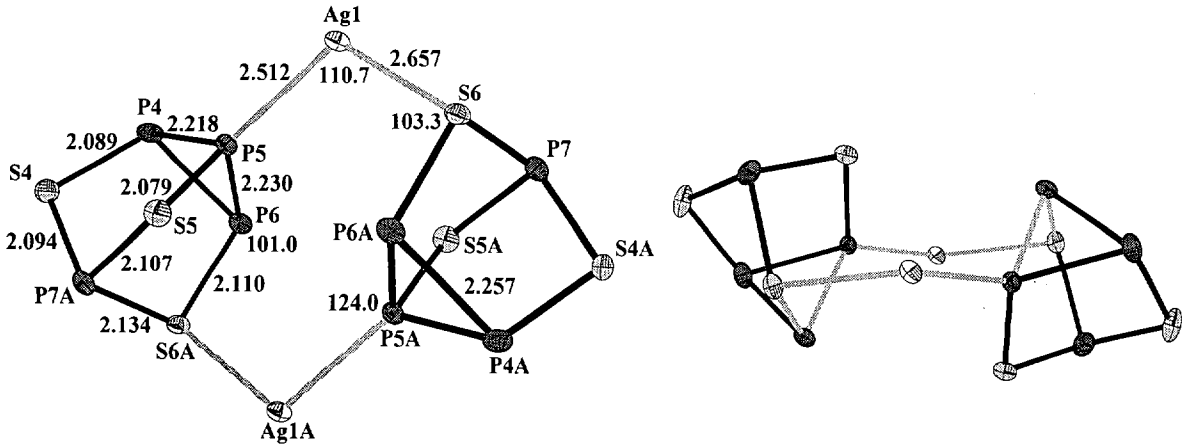
S-Figure 5: Structural parameters of isomer 2 in **1b**. Distances are given in Å, standard deviations are 0.005Å for Ag-P distances, the rest is given in the figure.

*c) The 6 membered ring within **2***



S-Figure 6: Structural parameters of the planar six membered ring in **2**. Distances are given in Å, bond angles in °. Standard deviations are 0.001Å for distances and 0.1° for bond angles. Bonds to silver are drawn in gray and those within the P_4S_3 cage in black.

d) The 8 membered ring within ***2***



S-Figure 7: Structural parameters of the slightly puckered eight membered ring in **2**. Distances are given in Å, bond angles in °. Standard deviations are 0.001Å for distances and 0.1° for bond angles. Bonds to silver are drawn in gray and those within the P_4S_3 cage in black.

Complete Computed Raman Frequencies and Experimental Frequencies of the Anions

S-Table 1: Experimental Raman frequencies of the $Al(hfip)_4^-$ and $Al(pftb)_4^-$ anions in **1-2** in comparison to the Li salts.[i]

	$LiAl(hfip)_4$[i]	**1**	**2**	$LiAl(pftb)_4$[i]
Assign.	Exp. (%)	Exp. (%)	Exp. (%)	Exp. (%)
$Al(OR)_4^-$	2955 (100)	2927 (17)		
$Al(OR)_4^-$	1390 (15)	1380 (5)		
$Al(OR)_4^-$	1295 (10)	1351 (3)		
$Al(OR)_4^-$	1200 (11)	1231 (2)		
$Al(OR)_4^-$	1129 (4)	1127 (3)		
$Al(OR)_4^-$	1098 (7)			
$Al(OR)_4^-$	855 (82)	860 (16)	796 (15)	801 (70)
$Al(OR)_4^-$	766 (28)	765 (13)	744 (15)	745 (90)
$Al(OR)_4^-$	750 (18)			
$Al(OR)_4^-$	730 (7)			
$Al(OR)_4^-$	703 (10)	716 (4)		
$Al(OR)_4^-$	689 (9)	696 (7)	572 (4)	571 (25)
$Al(OR)_4^-$		572 (4)	561 (5)	
$Al(OR)_4^-$	533 (16)	535 (3)	536 (9)	538 (40)
$Al(OR)_4^-$	523 (15)	523 (4)		
$Al(OR)_4^-$	484 (4)			
$Al(OR)_4^-$	330 (41)	332 (10)	321 (15)	326 (100)
$Al(OR)_4^-$	298 (10)	within P_4S_3	242 (14)	234 (20)
$Al(OR)_4^-$	218 (13)	within P_4S_3		

Calculated vibrational frequencies of the 6 ring

Sym.	wavenumber cm^{-1}	IR (%) km/mol	selection rules IR	RAMAN
bu	14.82	0.01620	YES	NO
au	30.41	0.03859	YES	NO
ag	37.81	0.00000	NO	YES
ag	47.86	0.00000	NO	YES
bg	53.23	0.00000	NO	YES
bg	60.37	0.00000	NO	YES
au	61.33	0.17956	YES	NO
bu	76.52	0.44338	YES	NO
au	79.74	0.40855	YES	NO
ag	104.77	0.00000	NO	YES
bg	120.06	0.00000	NO	YES
bu	149.29	4.05055	YES	NO
bg	183.88	0.00000	NO	YES
au	183.96	0.61184	YES	NO
bu	204.46	7.10479	YES	NO
ag	204.63	0.00000	NO	YES
bg	207.09	0.00000	NO	YES
au	207.51	3.94449	YES	NO
bu	284.80	1.32155	YES	NO
ag	286.15	0.00000	NO	YES
bg	293.07	0.00000	NO	YES
au	293.47	0.25186	YES	NO
bu	326.09	9.56722	YES	NO
ag	326.49	0.00000	NO	YES
bu	328.65	15.34712	YES	NO
ag	329.90	0.00000	NO	YES
bg	356.71	0.00000	NO	YES
au	358.38	0.02570	YES	NO
ag	360.91	0.00000	NO	YES
bu	361.08	10.23675	YES	NO
au	367.45	19.11959	YES	NO
bg	367.56	0.00000	NO	YES
bu	368.82	21.14059	YES	NO
ag	368.82	0.00000	NO	YES
bu	439.16	3.93428	YES	NO
ag	441.03	0.00000	NO	YES
bu	467.43	15.88925	YES	NO
ag	468.06	0.00000	NO	YES
bu	494.28	3.70101	YES	NO
ag	495.39	0.00000	NO	YES
bg	501.07	0.00000	NO	YES
au	502.98	4.28719	YES	NO

Calculated vibrational frequencies of the 8 ring

Sym.	wavenumber cm^{-1}	IR (%) km/mol	selection rules IR	RAMAN
au	25.05	0.09003	YES	NO
ag	37.07	0.00000	NO	YES
au	38.71	0.65074	YES	NO
ag	42.92	0.00000	NO	YES
ag	52.61	0.00000	NO	YES
au	56.68	0.81556	YES	NO
ag	65.73	0.00000	NO	YES
au	74.41	1.01709	YES	NO
au	82.04	0.26298	YES	NO
ag	102.99	0.00000	NO	YES
ag	128.99	0.00000	NO	YES
au	142.84	0.38304	YES	NO
ag	187.17	0.00000	NO	YES
au	189.38	1.37459	YES	NO
ag	210.72	0.00000	NO	YES
au	212.28	4.37675	YES	NO
au	263.77	9.27367	YES	NO
ag	265.10	0.00000	NO	YES
ag	272.60	0.00000	NO	YES
au	274.16	9.85793	YES	NO
au	289.69	5.34059	YES	NO
ag	290.79	0.00000	NO	YES
ag	310.68	0.00000	NO	YES
au	310.81	19.32124	YES	NO
au	326.62	0.51616	YES	NO
ag	326.63	0.00000	NO	YES
ag	332.19	0.00000	NO	YES
au	334.47	7.74750	YES	NO
au	345.25	8.28884	YES	NO
ag	346.50	0.00000	NO	YES
au	384.13	21.52353	YES	NO
ag	384.64	0.00000	NO	YES
ag	393.20	0.00000	NO	YES
au	393.83	17.61382	YES	NO
ag	415.07	0.00000	NO	YES
au	415.92	5.23028	YES	NO
au	438.62	8.55929	YES	NO
ag	439.39	0.00000	NO	YES
au	451.51	4.45804	YES	NO
ag	451.60	0.00000	NO	YES
ag	472.69	0.00000	NO	YES
au	473.59	0.57142	YES	NO

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[i] I. Krossing, *Chem. Eur. J.* **2001**, *7*, 490.