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TECHNICAL ARTICLE

Synthesis and crystal structure of $(Ag,Pd)_{22}Se_6$

F. Laufek,[1,a] A. Vymazalová,[1] D.A. Chareev,[2] A.V. Kristavchuk,[2,4] J. Drahokoupil,[3] and M.V. Voronin[2]
[1]*Czech Geological Survey, Geologická 6, 152 00 Praha 5, Czech Republic*
[2]*Institute of Experimental Mineralogy RAS, Chernogolovka, Moscow region, 142432 Russia*
[3]*Institute of Physics, ASCR v.v.i., Na Slovance 2, 182 21 Prague 8, Czech Republic*
[4]*University of Dubna, Universitetskaja 19, Dubna 141 980, Russia*

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The $(Ag,Pd)_{22}Se_6$ phase was synthesized from individual elements by silica glass tube technique and structurally characterized from powder X-ray diffraction data. The $(Ag,Pd)_{22}Se_6$ phase crystallizes in $Fm\bar{3}m$ symmetry, unit-cell parameters: $a = 12.3169(2)$ Å, $V = 1862.55(5)$ Å^3, $Z = 4$, and $D_c = 10.01$ g/cm^3. The crystal structure of the $(Ag,Pd)_{22}Se_6$ phase represents a stuffed $3a.3a.3a$ superstructure of the Pd structure (fcc), where only 4 from 108 available octahedral holes are occupied. Its crystal structure is related to the $Cr_{23}C_6$ structure type. © *2013 International Centre for Diffraction Data.*
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Key words: $(Ag,Pd)_{22}Se_6$, Rietveld refinement, crystal structure, Ag–Pd–Se system, X-ray powder diffraction data

I. INTRODUCTION

Recently, we reported a crystal structure study of a new silver palladium selenide with metallic behaviour, $AgPd_3Se$ (Laufek *et al.*, 2011). The crystal structure of this compound is formed by two kinds of interpenetrating networks of Ag, Pd, and Se atoms. Another known silver palladium selenide is the $Ag_2Pd_3Se_4$ phase, which is known from natural occurrence as a mineral chrisstanleyite (Paar *et al.*, 1998). Its crystal structure is composed of two distinct frameworks of polyhedra (elongated $AgSe_4$ tetrahedra and $PdSe_4$ squares) that interpenetrate and support each other (Topa *et al.*, 2006). During the further research of phase relations in the Ag–Pd–Se system, another ternary metal-rich selenide–the $(Ag,Pd)_{22}Se_6$ phase–was described. According to Vymazalová *et al.* (2012), this phase crystallizes in the $Fm\bar{3}m$ space group and forms a solid solution showing an extensive substitution of silver for palladium, whereas the selenium content is almost constant.

Since no crystal structure data of the $(Ag,Pd)_{22}Se_6$ phase are hitherto known, we carried out a crystal structure study of this compound. Powder diffraction data up to 140°2θ (Co$K\alpha$) are also reported. Part of this work was presented in a conference abstract (Laufek *et al.*, 2012).

II. EXPERIMENTAL

The ternary $(Ag,Pd)_{22}Se_6$ phase was prepared, using solid-state techniques, in silica glass tubes. Pure elements (silver 99.999%, selenium 99.999%, and palladium 99.95%) were used as starting materials. The evacuated tube with carefully weighted charge was at first annealed at 650°C for 2 days. The charge was grinded in acetone and again heated at 500°C for 35 days, after which the sample was quenched in a cold-water bath.

Chemical analyses were carried out on a Cameca SX-100 microprobe, in the wave-length-dispersion mode using a focused beam (size 1–2 μm). Accelerating voltage was set to 15 keV and the beam current to 10 nA. The sample was analysed using Pd L_α, Ag L_β, and Se L_α lines; pure metals were used as standards. The data were collected on several different crystals and then averaged. The chemical analysis yielded an overall composition of $(Ag_{10.61(7)}Pd_{11.72(4)})_{\Sigma 22.33}Se_{6.00}$ (based on 6 Se per formula unit).

III. STRUCTURE REFINEMENT

The powder X-ray diffraction pattern used for the structure determination was collected in Bragg-Brentano geometry on an X'Pert Pro PANalytical diffractometer, equipped with an X'Celerator detector using Co$K\alpha$ radiation. To minimize background, the specimen was placed on a flat low-background silicon wafer. The data were collected in the range from 10 to 140°2θ. A full-width at half maximum of 0.074°2θ was obtained at 44.339°2θ showing good crystallinity of the studied sample.

The crystal structure of $(Ag,Pd)_{22}Se_6$ was refined by the Rietveld method for powder X-ray diffraction data using the FullProf program (Rodriguez-Carvajal, 1990). A pseudo-Voigt function was used to generate the line shape of the diffraction peaks; the background was determined by linear interpolation between consecutive breakpoints in the powder pattern. A preliminary Rietveld refinement using the crystal structure of Pd ($Fm\bar{3}m$, $a = 4.1056$ Å, Pd atom at 4a position) (Maeland and Flanagan, 1964) fitted the most intensive reflections ($R_p = 7.86\%$, $R_{wp} = 14.3\%$) in the powder diffraction pattern; however, many other relative weak reflections were not fitted by this simple cubic model. Indexing of the powder pattern by means of the program DICVOL06 (Louër and Boultif, 2007) revealed that all reflections can be fitted by a cubic supercell with $a' = 3a$ ($a = 12.31$ Å). Therefore, the $3a.3a.3a$ superstructure of Pd (fcc structure)

[a]Author to whom correspondence should be addressed. Electronic mail: frantisek.laufek@geology.cz

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was created using the Wycksplit program from Bilbao Crystallographic Server (Kroumova *et al.*, 1998). This superstructure with $Fm\bar{3}m$ symmetry is a *k*-subgroup at index 27 of the $Fm\bar{3}m$ space group; the 4*a* crystallographic position in the Pd structure is split into the 4*a*, 24*e*, 32*f,* and 48*h* positions. Since it is nearly impossible to distinguish between Ag and Pd atoms in the conventional powder diffraction experiments, all metallic positions in the superstructure were treated as Ag/Pd mix positions with 0.5/0.5 occupancy. In order to comply with the measured stoichiometry of $(Ag_{10.61(7)}Pd_{11.72(4)})_{\Sigma 22.33}Se_{6.00}$, the 24*e* position was assigned as Se; the 4*a*, 32*f,* and 48*h* positions as Ag/Pd mix positions. The stoichiometry of this structure model is $(Ag,Pd)_{21}Se_6$. The subsequent Rietveld refinement converged to $R_p = 6.12\%$, $R_{wp} = 10.8\%$. Nevertheless the difference Fourier map revealed one large positive peak (32.2 e A^{-3}) at coordinates ½, 0, 0 (i.e. at the 4*b* position) suggesting that some atoms are missing in the current structure model. From the comparison of stoichiometry of the current structure model $(Ag,Pd)_{21}Se_6$ and the measured chemical composition of $(Ag_{10.61(7)}Pd_{11.72(4)})_{\Sigma 22.33}Se_{6.00}$, it was evident that this 4*b* position corresponds to the next Ag/Pd mix site. Thus, this position was assigned as next Ag/Pd mixed position in subsequent refinements, during which the values of R_p and R_{wp} significantly decreased to 3.85 and 5.06%, respectively.

Finally, 17 parameters including six profile and eight structural variables were refined. The maximum and minimum peaks in the final difference Fourier map were 1.21 and −1.85 e A^{-3}. The structure derived chemical composition $(Ag,Pd)_{22}Se_6$ is in a good agreement with the chemical composition of $(Ag_{10.61(7)}Pd_{11.72(4)})_{\Sigma 22.33}Se_{6.00}$ measured by electron microprobe. The details of the final refinement are summarized in Table I, the refined atomic coordinates and isotropic displacement parameters are given in Table II. Figure 1 shows the final Rietveld plot.

TABLE I. Experimental conditions.

Instrument	PANalytical X'Pert Pro
Radiation	Co$K\alpha_1$, Co$K\alpha_2$
Detector	X'Celerator
Soller slits	0.02 rad
Divergence slit	0.25°
Anti-scatter slit	0.5°
Step width	0.02°
Specimen form	Powder
Specimen particle size	Ground in agate mortar and pestle to <15 μm
Specimen holder	"Zero" background
Specimen motion	Spinning: 1 r s^{-1}

IV. RESULTS AND DISCUSSION

The powder diffraction data are listed in Table III. The observed values of diffraction positions, *d*-spacing, and intensities were extracted by the *XFIT* program (Coelho and Cheary, 1997) employing the split Pearson VII profile function. $2\theta_{obs}$ and d_{obs} were corrected for the refined zero-point shift of 0.027°2θ.

The refined structure has four cation sites, all of which were refined as mixed Ag/Pd sites, and one Se position. All atomic sites are in different types of special positions, with 0 and 1 degree of freedom for positional parameters. The cation sites were labelled from M1 to M4 because of their Ag/Pd mixed character; all occupancy parameters for Ag and Pd were set to 0.5/0.5.

The crystal structure of $(Ag,Pd)_{22}Se_6$ can be described as a stuffed 3*a*.3*a*.3*a* superstructure of cubic close packing of atoms, where only four from 108 octahedral holes are occupied. The corresponding group–subgroup relation is $Fm\bar{3}m\,\frac{k27}{3a}\,Fm\bar{3}m$ and is shown in Figure 2.

The unit cell of $(Ag,Pd)_{22}Se_6$ as well as the selected coordination polyhedra of all atoms are presented in Figure 3. The M1 site is coordinated by 12 M4 atoms in a cuboctahedral arrangement. These cuboctahedra are regular with the M(4)–M(4) edge distance of 2.922(2) Å. The M2 atoms are in the centre of regular octahedra with M2–Se distances of 2.664(1) Å. These $[M(2)Se_6]$ octahedra are isolated from each other and alternate with $[M(1)M(4)_{12}]$ cuboctahedra in the NaCl-type fashion. The M3 and M4 atoms also show cuboctahedral coordination, however, considerably distorted. The Se atoms are inside monocapped tetragonal antiprism built by the M3, M4 and M4 positions. As is also shown in Figure 4(a), the M3 atoms also form regular cubes, which are centred by the M2 atoms. However, there are no short M4–M2 interactions (3.587 Å). The Se atoms are placed slightly above the centres of the faces of these $[M(3)_8]$ cubes (Figure. 4a). It is interesting to note that the edge-length of the $[M(3)_8]$ cubes (4.142 Å) is very close to the thickness of the $[M(1)M(4)_{12}]$ cuboctahedra (4.134 Å). The selected bond lengths are summarized in Table IV.

The crystal structure of the $(Ag,Pd)_{22}Se_6$ represents a unique structure; no exact structural analogues were found in the ICSD database (Fachinformationszentrum Karlsruhe, 2012). However, it shows close structural relation to the $Cr_{23}C_6$ type structure (Bowman *et al.*, 1972). Both phases exhibit the same symmetry ($Fm\bar{3}m$) and very similar stoichiometry (Pearson symbols are *cF*112 and *cF*116, respectively). In both compounds, the electronegative atoms (C or Se) occupy the position 24*e*, while the 4*a*, 32*f,* and

TABLE II. Refined parameters for $(Ag,Pd)_{22}Se_6$ [room temperature, space group $Fm\bar{3}m$, $a = 12.3169(2)$ Å, $V = 1862.55(5)$ Å^3, $Z = 4$, $D_c = 10.01$ g/cm^3, $R_p = 3.85\%$, $R_{wp} = 5.06\%$, and $R_B = 3.51\%$].

Atom	Site	*X*	*y*	*Z*	B_{iso} (Å^2)
M1	4*a*	0	0	0	0.48(9)
M2	4*b*	½	½	½	0.60(8)
M3	32*f*	0.6681(1)	0.6681(1)	0.6681(1)	0.72(4)
M4	48*h*	0	0.8322(1)	0.8322(1)	0.87(4)
Se(1)	24*e*	0.7163(2)	0	0	0.93(5)

The M1–M4 sites represent the Ag/Pd mixed positions with 0.5/0.5 occupancy.

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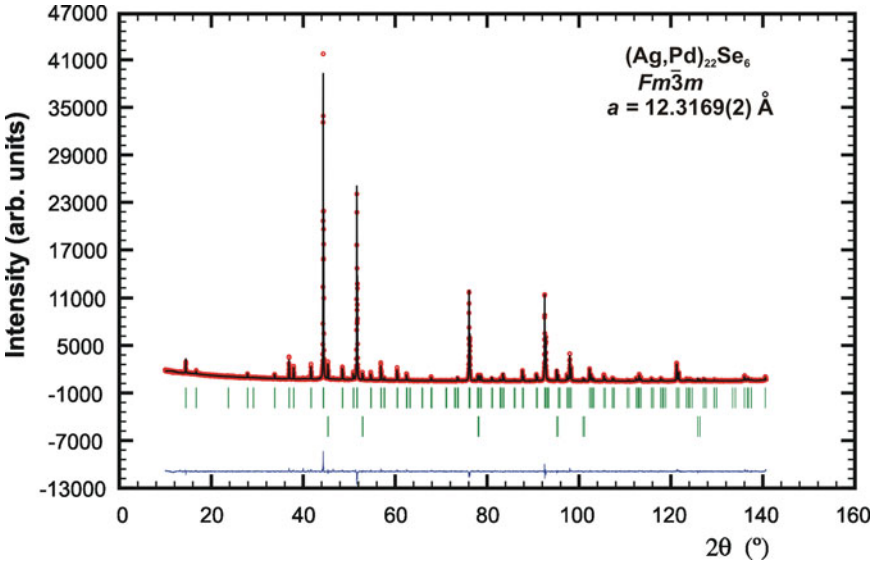


Figure 1. Observed (circles), calculate (solid line) and difference Rietveld profiles for $(Ag,Pd)_{22}Se_6$. The upper reflection bars correspond to $(Ag,Pd)_{22}Se_6$ and the lower bars to 3 mass percent (Ag,Pd) alloy impurity.

TABLE III. Powder diffraction data for $(Ag,Pd)_{22}Se_6$ (Co$K\ \alpha$ radiation). Reflection with I_{obs} and $I_{calc} < 0.5\%$ are not shown in the table.

h	k	l	$2\theta_{obs}$(°)	d_{obs}(Å)	I_{obs}	$2\theta_{calc}$(°)	d_{calc}(Å)	I_{calc}	$2\theta_{obs}-2\theta_{calc}$
1	1	1	14.462	7.1062	2.9	14.452	7.1111	3.1	0.010
2	0	0	n			16.702	6.1586	0.7	
3	1	1	27.898	3.7105	1.0	27.874	3.7137	1.1	0.024
4	0	0	33.772	3.0794	1.4	33.774	3.0792	1.4	−0.002
3	3	1	36.911	2.8255	6.5	36.908	2.8257	6.1	0.003
4	2	0	37.904	2.7541	3.8	37.903	2.7542	3.6	0.001
4	2	2	41.684	2.5140	4.4	41.681	2.5142	4.0	0.003
3	3	3	44.340	2.3703	100.0	44.339	2.3704	100.0	0.001
4	4	0	48.511	2.1773	4.0	48.511	2.1773	4.0	0.000
5	3	1	50.890	2.0819	2.1	50.888	2.0819	2.1	0.002
4	4	2	51.665	2.0527	62.0	51.663	2.0528	8.3	0.002
6	0	0				51.663	2.0528	59.7	
6	2	0	54.688	1.9473	2.2	54.683	1.9475	2.2	0.005
5	3	3	56.879	1.8782	6.4	56.875	1.8783	5.4	0.004
6	2	2				57.594	1.8569	1.0	
4	4	4	60.418	1.7777	4.0	60.414	1.7778	4.0	0.004
7	1	1	62.481	1.7247	1.9	62.479	1.7247	1.8	0.002
5	5	3	67.805	1.6036	1.1	67.809	1.6035	1.1	−0.004
6	4	4	73.588	1.4934	0.9	73.574	1.4936	0.9	0.014
6	6	0	76.076	1.4516	34.2	76.079	1.4516	38.2	−0.003
7	5	1	77.934	1.4223	1.1	77.940	1.4222	1.0	−0.006
6	6	2	78.559	1.4128	2.3	78.557	1.4128	2.6	0.002
8	4	0	81.010	1.3771	1.4	81.013	1.3771	1.4	−0.003
9	1	1	82.831	1.3521	1.0	82.844	1.3520	1.0	−0.013
8	4	2	83.451	1.3439	2.7	83.453	1.3439	3.1	−0.002
9	3	1	87.692	1.2912	4.6	87.697	1.2912	4.8	−0.005
8	4	4	90.717	1.2571	3.0	90.719	1.2571	3.3	−0.002
7	7	1	92.527	1.2380	40.0	92.533	1.2379	1.8	−0.006
9	3	3				92.533	1.2379	39.8	
9	5	1	97.373	1.1909	2.7	97.387	1.1907	2.4	−0.014
7	7	3				97.387	1.1907	0.5	
6	6	6	97.991	1.1853	12.5	97.997	1.1852	12.5	−0.006
9	5	3	102.290	1.1486	6.3	102.296	1.1486	6.4	−0.006
10	4	0	102.901	1.1437	1.2	102.915	1.1436	1.2	−0.014
10	4	2	105.400	1.1244	3.1	105.408	1.1244	2.9	−0.008
11	1	1	107.288	1.1106	1.4	107.298	1.1106	0.5	−0.010
7	7	5				107.298	1.1106	0.9	
9	5	5	112.434	1.0762	1.2	112.440	1.0761	1.4	−0.006
8	8	2	113.085	1.0721	3.6	113.095	1.0721	0.5	−0.010
10	4	4				113.095	1.0721	2.9	
8	6	6	115.737	1.0562	1.1	115.750	1.0562	1.0	−0.013
9	7	3	117.776	1.0447	1.5	117.781	1.0447	0.7	−0.005
11	3	3				117.781	1.0447	0.5	
8	8	4	121.251	1.0264	11.0	121.254	1.0264	1.5	−0.003
12	0	0				121.254	1.0264	9.3	

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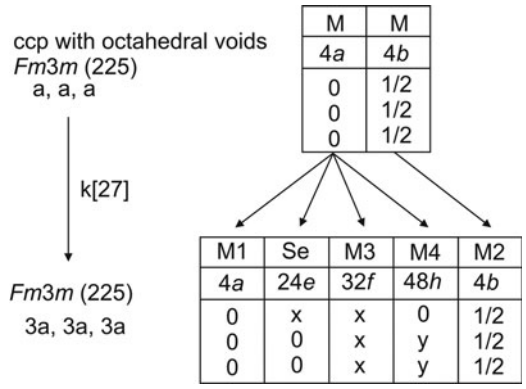


Figure 2. Group–subgroup relation between $(Ag,Pd)_{22}Se_6$ and cubic close packing (ccp).

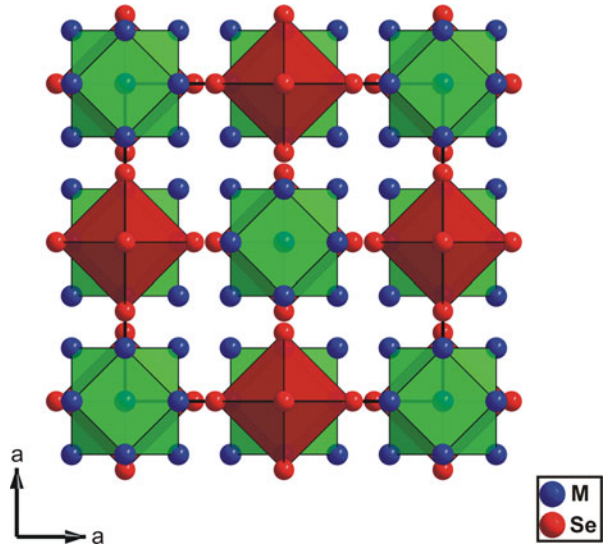


Figure 3. Polyhedral representation of $(Ag,Pd)_{22}Se_6$ crystal structure emphasizing the [M(1)M(4)12] cuboctahedra and [M(2)Se6] octahedra (M = Ag/Pd mix sites). Unit-cell edges are highlighted.

TABLE IV. Selected interatomic distances (Å) for $(Ag,Pd)_{22}Se_6$. The M1–M4 sites represent the Ag/Pd mixed positions with 0.5/0.5 occupancy.

M1–M4	12×	2.923(1)	M4–Se1	2×	2.512(2)
M2–Se1	6×	2.664(1)	– M4	1×	2.864(2)
M3–M3	3×	2.853(2)	– M3	4×	2.893(2)
– M4	6×	2.893(2)	– M1	1×	2.923(2)
– Se1	3×	2.988(2)	– M4	4×	2.922(2)
Se1–M4	4×	2.512(2)			
– M2	1×	2.664(3)			
– M3	4×	2.988(1)			

48*h* positions are occupied by electropositive atoms (Cr or Ag and Pd). The characteristic distinction between these two structures is different occupancy of the 4*b* and 8*c* positions. As is evident from Figure 4, the 4*b* position is occupied in the $(Ag,Pd)_{22}Se_6$ structure (M2 atoms in centres of the $[M(3)_8]$ cubes), whereas the 8*c* position is vacant. Contrary to that, the $Cr_{23}C_6$ structure has exactly opposite occupation scheme of these two positions; the vacant 4*b* position (note the empty cubes in Figure 4b) and occupied the 8*c* position. Remarkable is also the difference in the ratio between the edge-length of the cubes and thickness of the cuboctahedra (see Figure 4). This ratio is 0.70 for the empty cube in $Cr_{23}C_6$, while the ratio for the $[M(3)_8]$ cube filled by the M2 atoms is 1.00. As discussed in detail by Adelsberger and Jansen (1999), the $Cr_{23}C_6$ structure type also shows the group–subgroup relation to the cubic close packing of atoms.

It is also worth mentioning that the Se atoms in the $(Ag,Pd)_{22}Se_6$ structure form an octahedral network (Figure 5a). This network consists of large and small corner-sharing octahedra, which alternate in the NaCl-type fashion. The M1 (4*a*) and M2 (4*b*) atoms are located at the centres of large and small octahedra, respectively. As shown in Figure 5b, analogical arrangement of C atoms was described for $Cr_{23}C_6$-type structures by Ohodnicky *et al.* (2008). However, while the large octahedra have the Cr atoms in their centres, the small octahedra are vacant.

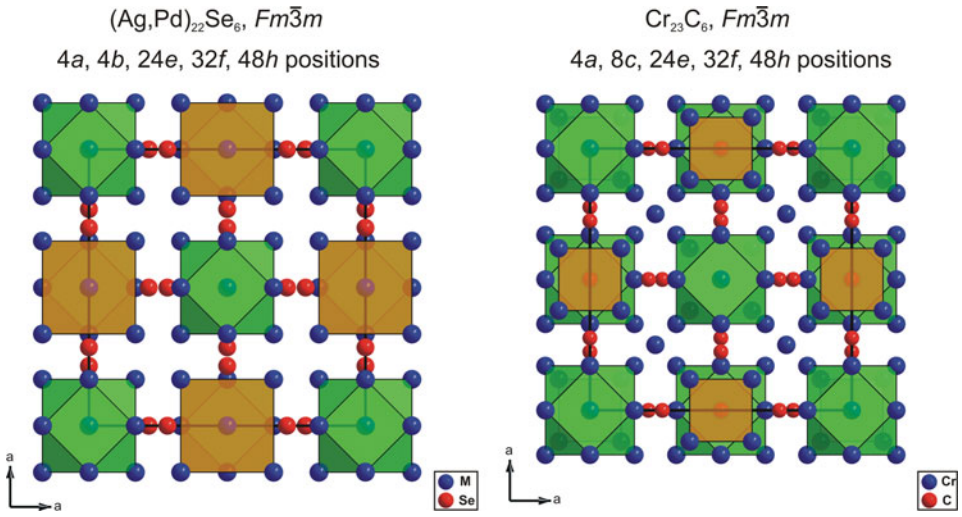


Figure 4. Comparison of $(Ag,Pd)_{22}Se_6$ and $Cr_{23}C_6$ (Bowman *et al.*, 1972) crystal structures. The [M(3)8] cubes (orange) and [M(1)M(4)12] cuboctahedra (green) are emphasized (M = Ag/Pd or Cr). Note the difference (4*a* vs. 8*c*) in the occupied Wyckoff positions in both structures. Unit-cell edges are highlighted.

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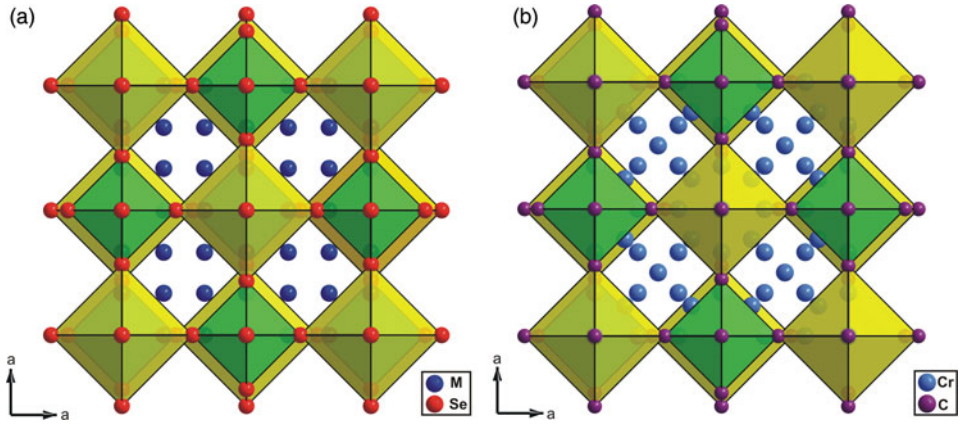


Figure 5. Polyhedral representation of the (a) $(Ag,Pd)_{22}Se_6$ and (b) $Cr_{23}C_6$ crystal structures (Bowman *et al.*, 1972). The corner-sharing octahedral networks of Se and C atoms are shown. (M = Ag/Pd).

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