Supplementary Information

Dependence of the crystal structure of Prussian blue on the occupation of interstitial sites

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Table 1: Effective ionic radii of relevant ions. Adapted from [1].

Ion	Efective ionic radii (pm)
Li^+	76
Na^+	102
K^+	138
Rb^+	152
H_3O^+	100
$[Fe(CN)_6]^{3-}$	357

Tables 2, 3 and 4 present the relative change in volume ΔV, distortion energy ΔE and enthalpy of formation ΔH_f^o. ΔV is the variation in volume related to the cubic cell for each cation, in percentage. ΔE is the difference between the energy of a configuration and the total energy of the cubic cell, for each cation. The enthalpy of formation, ΔH_f^o, was calculated using the following equations:

Soluble PB:

$$\Delta H_f^o = E(PB_s) - E(xA) - E\left(Fe^{3+}\right) - E\left(Fe^{2+}\right) - E(6CN) \tag{1}$$

Soluble PW:

$$\Delta H_f^o = E(PW_s) - E(xA) - E\left(Fe^{2+}\right) - E\left(Fe^{2+}\right) - E(6CN) \tag{2}$$

Insoluble PB:

$$\Delta H_f^o = E(PB_i) - E\left(Fe^{3+}\right) - 0.75E\left(Fe^{2+}\right) - 0.75E(6CN) - 1.5E(H_2O) \tag{3}$$

Insoluble PW:

$$\Delta H_f^o = E(PW_i) - E(A) - E\left(Fe^{2+}\right) - 0.75E\left(Fe^{2+}\right) - 0.75E(6CN) - 1.5E(H_2O), \tag{4}$$

where A is the ionic species, and $E(PB)$ or $E(PW)$ is the energy of the compound per unit of formula.

Table 2: Volume, relative energy and enthalpy of formation for soluble Prussian Blue. The Wyckoff positions in the table are related to the initial position of the ions in the cubic cell.

Cation	Site	Space group	$V(\mathring{A}^3)$	$\Delta V(\%)$	$E(eV)$	$\Delta E(eV)$	$\Delta H_f^o(eV/atom)$
Li	8*c*	$F\bar{4}3m$	1042.24	0	4.355	0	−1.898
	24d	**Immm**	**1036.61**	**−0.54**	**0**	**−4.355**	**−1.971**
	$32f'$	$R3m$	1047.24	0.48	1.930	−2.425	−1.938
	32*f*	$R3m$	1059.53	1.66	0.603	−3.752	−1.960
Na	8*c*	$F\bar{4}3m$	1043.50	0	1.821	0	−1.946
	24d	**Immm**	**1062.13**	**1.79**	**0**	**−1.821**	**−1.976**
	$32f'$	$R3m$	1047.41	0.37	1.112	−0.709	−1.957
	32*f*	$R3m$	1055.87	1.19	0.766	−1.055	−1.963
K	8*c*	$F\bar{4}3m$	1049.58	0	0.178	0	−2.012
	24*d*	$Immm$	1097.96	4.61	3.021	2.843	−1.965
	$32f'$	$R3m$	1054.34	0.45	0.063	−0.114	−2.014
	32f	**R3m**	**1054.54**	**0.47**	**0**	**−0.178**	**−2.015**
Rb	8*c*	$F\bar{4}3m$	1053.46	0	0.123	0	−2.025
	24*d*	$Immm$	1118.36	6.16	5.440	5.317	−1.936
	32f′	**R3m**	**1057.48**	**0.38**	**0**	**−0.123**	**−2.027**
	32*f*	$R3m$	1055.04	0.15	0.150	0.027	−2.024

Table 3: Volume, relative energy and enthalpy of formation for soluble Prussian White

Cation	Site	Space group	$V(\mathring{A}^3)$	$\Delta V(\%)$	$E(eV)$	$\Delta E(eV)$	$\Delta H_f^o(eV/atom)$
Li	8*c*	$Fm\bar{3}m$	1042.69	0	8.330	0	−1.721
	24*d*	$I4/mmm$	1051.78	0.87	1.994	−6.336	−1.820
	$32f'$	$R\bar{3}m$	1042.90	0.02	2.481	−5.849	−1.812
	32f	**R$\bar{3}$m**	**1071.28**	**2.74**	**0**	**−8.330**	**−1.851**
Na	8*c*	$Fm\bar{3}m$	1045.84	0	2.625	0	−1.810
	24d	**I4/mmm**	**1081.96**	**3.45**	**0**	**−2.625**	**−1.851**
	$32f'$	$R\bar{3}m$	1044.65	−0.11	1.101	−1.524	−1.834
	32*f*	$R\bar{3}m$	1065.47	1.88	0.471	−2.154	−1.843
K	8*c*	$Fm\bar{3}m$	1057.05	0	0.004	0	−1.934
	24*d*	$I4/mmm$	1168.91	10.58	6.146	6.142	−1.838
	$32f'$	$R\bar{3}m$	1056.44	−0.06	0.042	0.038	−1.934
	32f	**R$\bar{3}$m**	**1056.91**	**−0.01**	**0**	**−0.004**	**−1.934**
Rb	**8c**	**Fm$\bar{3}$m**	**1065.34**	**0**	**0**	**0**	**−1.957**
	24*d*	$I4/mmm$	1236.22	16.04	11.085	11.085	−1.783
	$32f'$	$R\bar{3}m$	1064.89	−0.04	0.038	0.038	−1.956
	32*f*	$R\bar{3}m$	1065.32	0.002	0.005	0.005	−1.956

Table 4: Volume, relative energy and enthalpy of formation for the insoluble forms of Prussian Blue and Prussian White

Compound	Site	Space group	$V(\AA^3)$	$\Delta V(\%)$	$E(eV)$	$\Delta E(eV)$	$\Delta H_f^o(eV/atom)$
PB	–	$Pm\bar{3}$	1029.46	0	0	0	−1.317
K-PW	8*c*	$P23$	1061.04	0	1.778	0	−1.327
	24*d*	$P2/m$	1070.26	0.87	3.986	2.208	−1.293
	32f′	**R3**	**1050.84**	**−0.96**	**0**	**−1.778**	**−1.355**
	32*f*	$R3$	1055.82	−0.49	0.004	−1.774	−1.355
Na-PW	8*c*	$P23$	1045.68	0	4.963	0	−1.249
	24*d*	$P2/m$	1041.33	−0.42	2.554	−2.408	−1.286
	32*f′*	$R3$	1047.26	0.15	0.140	−4.823	−1.323
	32f	**R3**	**1039.07**	**−0.63**	**0**	**−4.963**	**−1.325**

References

[1] Alexander Kraft. Some considerations on the structure, composition, and properties of prussian blue: A contribution to the current discussion. *Ionics*, 27(6):2289–2305, 2021.