

Incorporation of Cyano Transition Metal Complexes in KCl Crystals—Experimental and Computational Studies

Damien J. Carter,^A Mark I. Ogden^{A,B} and Andrew L. Rohl^A

^A Nanochemistry Research Institute, Curtin University of Technology, GPO Box U 1987, Perth 6845, Australia.

^B Author to whom correspondence should be addressed (e-mail: m.ogden@curtin.edu.au).

Experimental and computational studies of the incorporation of hexacyanoferrate(II), hexacyanocobaltate(III), and hexacyanoferrate(III) into potassium chloride crystals are described. The experimental results showed that the extent of incorporation follows the trend hexacyanoferrate(II) \gg hexacyanoferrate(III) $>$ hexacyanocobaltate(III). Computational modelling produced replacement energies that match the experimental trend. The calculated geometry of the incorporated complexes was also found to match well with previous experimental results.

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Introduction

The incorporation of foreign molecules or ions in a growing crystal is a common phenomenon, despite the utility of crystallization as a purification method. Examples range from substitutions involving similar species, such as cation substitution in ionic solids, to systems where there is large disparity between the guest and the host lattice. Examples of the latter are often found in biomineralization, where nature achieves remarkable control of inorganic crystal growth, in part by interaction with protein molecules.^[1] Attractive examples are found in the many ionic solids that have been found to incorporate dye molecules.^[2] Contamination of crystalline products is also of relevance to many industrial processes. Incorporation of impurities impacts on product quality or complicates the disposal of by-products where, for example, toxic metals may be captured by otherwise innocuous materials.^[3]

One system of industrial significance is the doping of transition metal complexes into cubic halide crystals. In the production of salt by evaporation of saline water, hexacyanoferrate(II) is added to prevent caking.^[4] In the photographic industry, transition metal complexes are incorporated into the silver halide microcrystals that comprise photographic emulsions, which mediate the formation of the latent image.^[5] Computer simulations of impurity incorporation in crystals should result in improved understanding of the crystal–additive interactions. Baetzold and coworkers have successfully used molecular modelling to probe the doping of both NaCl and AgCl with hexacyanoferrate(II) and hexacyanoferrate(III) using interatomic potentials^[6] and more recently have repeated the work on NaCl using embedded cluster calculations,^[7] where the transition metal complex and the immediately surrounding lattice ions are simulated

quantum-mechanically whilst the rest of the lattice utilizes interatomic potentials.

In this paper, we report experimental and computational results probing the incorporation of three additives, hexacyanoferrate(II), hexacyanocobaltate(III), and hexacyanoferrate(III), into potassium chloride. The work to date in the literature has probed the preferred environments of the transition metal complexes in the crystal lattice, rather than focus on how much can be adsorbed. We chose these three additives as, although structurally similar, the first has a different charge to the other two and they all have different metal–carbon bond lengths. Thus, this series allows the effects of both charge and size on incorporation to be probed.

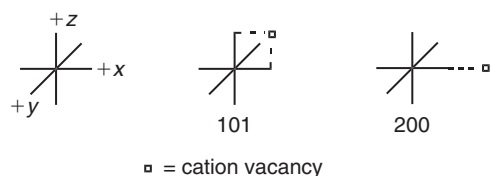
Results and Discussion

Crystal Growth

The aim of the experimental work was to determine the relative extent of incorporation of the three cyano complexes in potassium chloride crystals under slow growth conditions, for comparison with the computational results. A simple approach was taken where potassium chloride was crystallized in batches by controlled temperature reduction. The additive concentrations were varied from 10 to 500 ppm, and the levels of incorporation determined by analysis of the metal content of the crystals. Hexacyanoferrate(II), hexacyanocobaltate(III), and hexacyanoferrate(III) were all found to incorporate into the crystal lattice. The results are summarized in Table 1. It is clear that the charge of the complex has a significant effect, with the iron(II) complex incorporated at levels an order of magnitude higher than the iron(III) and cobalt(III) complexes. The cobalt(III) complex is incorporated at levels consistently less than that of the iron(III) complex.

Table 1. Experimentally determined incorporation of $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Co}(\text{CN})_6]^{3-}$, and $[\text{Fe}(\text{CN})_6]^{3-}$ into KCl

Initial additive concentration [ppm]	Concentration of complex in KCl [mg g^{-1}]		
	$\text{K}_4[\text{Fe}(\text{CN})_6]$	$\text{K}_3[\text{Fe}(\text{CN})_6]$	$\text{K}_3[\text{Co}(\text{CN})_6]$
10	0.11 ± 0.01	0.05 ± 0.01	0.03 ± 0.01
50	0.61 ± 0.06	0.09 ± 0.01	0.05 ± 0.01
100	1.17 ± 0.12	0.11 ± 0.01	0.07 ± 0.01
250	2.87 ± 0.29	0.25 ± 0.02	0.12 ± 0.01
500	3.71 ± 0.37	0.35 ± 0.03	0.28 ± 0.03

**Fig. 1.** The two possible cation vacancy configurations when $[\text{Fe}(\text{CN})_6]^{4-}$ is substituted into KCl.

Incorporation of cyano complexes into potassium chloride has been reported previously with an emphasis on spectroscopic characterization of the complex,^[8–12] and the effect of hexacyanoferrate(II/III) on the morphology of sodium chloride is well known with the iron(III) complex inducing a change from cubic to octahedral, and the iron(II) complex causing dendritic growth.^[4] It is interesting to note that in the present work, cubic crystals were produced in all cases. This may be a result of growing crystals by temperature reduction rather than evaporation,* this observation requires further investigation but lies outside the scope of the work presented here. To our knowledge, the extent of incorporation of these cyano complexes has not previously been reported under consistent experimental conditions.

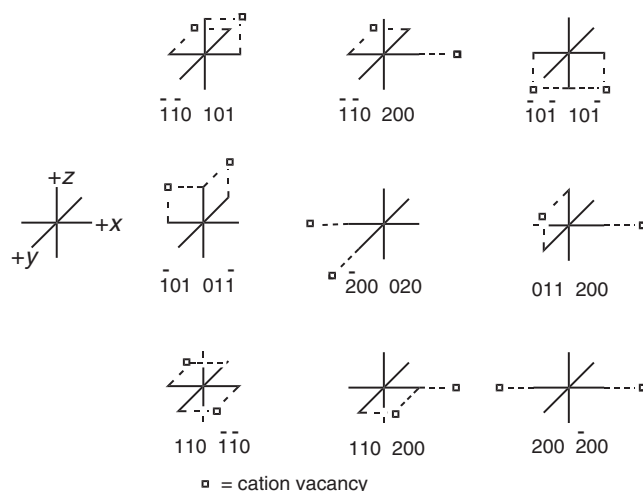
Computational Modelling

To create space for a hexacyano complex in the KCl lattice, a KCl_6^{5-} moiety must first be removed. As the complexes have charges of -3 (hexacyanoferrate(III) and hexacyanocobaltate(III)) and -4 (hexacyanoferrate(II)), potassium vacancies surrounding the incorporated complex must also be introduced. The hexacyanoferrate(II) complex requires a single vacancy and the others two vacancies. These vacancies will be more stable the closer they are to the complex, but this requirement still leads to two possibilities for the single vacancy, as shown in Figure 1, and nine possible divacancy configurations, Figure 2.

To assess the thermodynamics of incorporating a hexacyano complex into a KCl crystal, the replacement energy is calculated according to Equation (1)^[13]

$$E_{\text{replacement}} = (E_{\text{subs}} + nE_{\text{Cl}} + mE_{\text{K}} + nE_{\text{solv Cl}} + mE_{\text{solv K}}) - (E_{\text{cell}} + E_{\text{comp}} + E_{\text{solv comp}}) \quad (1)$$

where E_{subs} is the lattice energy of the KCl cell with either $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{CN})_6]^{3-}$, or $[\text{Fe}(\text{CN})_6]^{4-}$ substituted into

**Fig. 2.** The nine possible divacancy configurations when $[\text{Fe}(\text{CN})_6]^{3-}$ or $[\text{Co}(\text{CN})_6]^{3-}$ are substituted into KCl.

it, E_{Cl} is the energy of an isolated chloride ion, E_{K} is the energy of an isolated potassium ion, $E_{\text{solv Cl}}$ is the energy of solvation of a chloride ion, $E_{\text{solv K}}$ is the energy of solvation of a potassium ion, E_{cell} is the energy of the KCl cell without the hexacyano complex, E_{comp} is the energy of $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{CN})_6]^{3-}$, or $[\text{Fe}(\text{CN})_6]^{4-}$ in a vacuum, $E_{\text{solv comp}}$ is the energy of solvation of $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{CN})_6]^{3-}$, or $[\text{Fe}(\text{CN})_6]^{4-}$, n is the number of chloride ions removed from the lattice to accommodate the complex, and finally m is the number of potassium ions removed. The lattice energies and energies of the isolated ions were calculated using the GULP code^[14] utilizing the potentials and partial atomic charges discussed in the Experimental section. A $3 \times 3 \times 3$ supercell of KCl was used to keep the periodically repeating incorporated complexes from interacting with each other to any significant extent. The solvation energies were calculated as reported previously.^[13]

Tables 2 and 3 list the calculated replacement energies for the three different complexes in KCl. The hexacyanoferrate(II) vacancies are more stable (lowest energy) than the hexacyanoferrate(III) or hexacyanocobaltate(III) divacancies, with the 101 configuration producing the most stable configuration of all. For hexacyanoferrate(III) and hexacyanocobaltate(III), the order of most to least stable divacancies is the same. The hexacyanoferrate(III) complex is more stable for the two most stable divacancy configurations than the equivalent hexacyanocobaltate(III) configuration. Remarkably, for the rest the order of stability is reversed. The most stable divacancy configuration is the 110 $\bar{1}\bar{1}0$ and the least stable configuration is the 200 $\bar{2}00$ configuration. It should be noted that the energy differences between the 110 $\bar{1}\bar{1}0$ and $\bar{1}\bar{1}0$ 101 divacancy configurations of hexacyanoferrate(III) and hexacyanocobaltate(III) are all less than RT , suggesting that all four are equally likely at room temperature. Baetzold^[6] performed similar defect calculations in examining the incorporation of hexacyanoferrate(III) in sodium chloride. He also found that the 110 $\bar{1}\bar{1}0$ configuration was the most stable

* Crystals of KCl grown by evaporation of a drop of solution on a microscope slide did show changes in morphology consistent with the literature reports.

Table 2. The energy differences for replacing KCl_6^{5-} and associated vacancies with $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Co}(\text{CN})_6]^{3-}$, compared to the most stable vacancy

For the $110 \bar{1}\bar{1}0$ defect with $\text{K}_3[\text{Fe}(\text{CN})_6]$ the replacement energy was $-2368.68 \text{ kJ mol}^{-1}$

Defect	$\Delta E_{\text{replacement}} [\text{kJ mol}^{-1}]$	
	$\text{K}_3[\text{Fe}(\text{CN})_6]$	$\text{K}_3[\text{Co}(\text{CN})_6]$
$110 \bar{1}\bar{1}0$	0.00	0.91
$\bar{1}\bar{1}0 101$	0.97	1.09
$\bar{1}0\bar{1} 10\bar{1}$	22.68	19.13
$\bar{1}01 0\bar{1}\bar{1}$	22.87	21.89
$110 200$	29.74	27.50
$011 200$	36.29	33.52
$\bar{1}\bar{1}0 200$	41.83	39.89
$\bar{2}00 020$	72.21	67.49
$200 \bar{2}00$	109.46	104.48

Table 3. The energy differences for replacing KCl_6^{5-} and associated vacancies with $[\text{Fe}(\text{CN})_6]^{4-}$, compared to the most stable vacancy

For the 101 defect in $\text{K}_4[\text{Fe}(\text{CN})_6]$ the replacement energy was $-3744.30 \text{ kJ mol}^{-1}$

Defect	$\Delta E_{\text{replacement}} [\text{kJ mol}^{-1}]$
	$\text{K}_4[\text{Fe}(\text{CN})_6]$
101	0.00
200	27.32

but the next-most stable $\bar{1}\bar{1}0 101$ configuration within RT . Electron paramagnetic resonance (EPR) spectra measured by Wang, Meijers, and de Boer^[12] demonstrates that the $110 \bar{1}\bar{1}0$ configuration is the most stable in both NaCl and KCl, followed by $\bar{1}\bar{1}0 101$. Thus, although the interatomic potentials are not producing quantitative energy differences between configurations, they are giving a qualitatively correct description of the relative stabilities within these systems.

It is tempting to try and explain the replacement energy trends in terms of charge matching and lattice fit. To maintain charge neutrality with hexacyanoferrate(II), only one cation vacancy is required; hexacyanoferrate(III) and hexacyanocobaltate(III) require two cation vacancies. Energy is required to create these cation vacancies, so fewer vacancies will be energetically favourable. This is why the replacement energies for hexacyanoferrate(II) are the lowest. This correlates well with the experimental data, with hexacyanoferrate(II) incorporating to the greater extent. Hexacyanocobaltate(III) and hexacyanoferrate(III) have the same charge, so the difference in replacement energies could be related to the lattice fit. The Cl–K–Cl distance (including the ionic radius of chlorine) for potassium chloride is 9.92 \AA . The linear distance across N–C–M–C–N (including the van der Waals radius of nitrogen), where M represents Fe^{3+} and Co^{3+} , is 9.47 and 9.39 \AA respectively. This suggests that the best match is with hexacyanoferrate(III) and thus it should incorporate preferentially over hexacyanocobaltate(III). This agrees with the experimental data reported herein and the two calculated lowest energy configurations, but not for the less stable possibilities. This strongly suggests that even at the higher dosages, most of the hexacyanoferrate(III) and

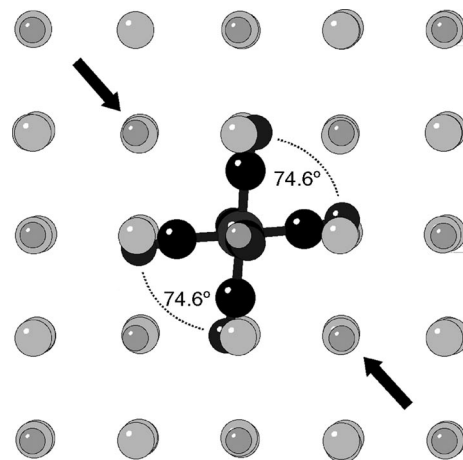


Fig. 3. View along the z -direction showing distortion of the cyanide ligands from octahedral when $[\text{Fe}(\text{CN})_6]^{3-}$ is relaxed within KCl, in the presence of 110 and $\bar{1}\bar{1}0$ defects (indicated by arrows).

hexacyanocobaltate(III) ions are incorporating with the two most stable divacancies. These results show that while simple geometric considerations can provide a preliminary guide to additive–crystal interactions, more detailed studies are required for accurate explanations and predictions. In this case, it would appear that the charge distribution (which varies between $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Co}(\text{CN})_6]^{3-}$) is an important factor in determining the replacement energies, and can compensate for differences in fit.

Another important result that can be obtained from molecular modelling calculations is the geometry of the minimized configurations. For hexacyanoferrate(III) with the most stable divacancy configuration, the cyano ligands are calculated to distort by 7.7° from octahedral, as shown in Figure 3. Experimental EPR measurements by Wang, Meijers, and de Boer^[12] showed distortions from octahedral symmetry of 6 – 8° . This close agreement with experimental results suggests that the interatomic potentials derived in this work are of high quality. The distortions for the hexacyanocobaltate(III) with the same defect configuration is 7.2° , that for hexacyanoferrate(II) with its most stable defect is 4.8° . The hexacyanoferrate(II) presumably distorts to a lesser extent than the other complexes because there is only one vacancy in the supercell.

Conclusion

A new set of interatomic potentials for hexacyano complexes has been developed, and utilized in the modelling of the incorporation of these complexes in the potassium chloride lattice. The results obtained were consistent with experimental data in terms of both levels of incorporation and geometry of the complexes within the crystal.

Experimental

Materials

KCl and $\text{K}_4[\text{Fe}(\text{CN})_6]$ (AR grade) were supplied by Ajax Chemicals. $\text{K}_3[\text{Co}(\text{CN})_6]$ and $\text{K}_3[\text{Fe}(\text{CN})_6]$ (AR grade) were supplied by the Aldrich Chemical Company.

Crystal Growth

Solutions of KCl (5.9 M, supersaturation ratio 1.13 at 30°C) with varying levels of additive were prepared. Additive concentrations used were

10, 50, 100, 250, and 500 ppm. Each solution (including blanks) was heated to approximately 80°C and filtered hot through a Gelman 0.2 µm membrane filter before being placed in a rotating waterbath. The temperature was held at 80°C for approximately 90 min and then ramped down from 80 to 30°C, at a rate of 5 min K⁻¹. The temperature was then held at 30°C for several hours. The crystals were isolated by filtration and washed with a sequence of saturated KCl solutions containing increasing amounts of ethanol. Some samples were crushed and rewashed before analysis to ensure macro-inclusions in the crystal were not biasing results. No significant changes in metal concentration were observed. Additive levels were determined by atomic absorption spectroscopy.

Generation of Potential Model

As the incorporation of [Co(CN)₆]³⁻ ions into any ionic lattice has not been previously modelled, we took the opportunity to develop a new set of interatomic potentials for hexacyano complexes. The charges on the atoms in each complex were calculated using the charge equilibration process of Rappè and Goddard.^[15] For the three complexes,

Table 4. Potential parameters used in this work

Harmonic Potentials				
		k [eV Å ⁻²]	r_0 [Å]	
Ferrocyanide	Fe ²⁺ -C	6.4961	2.0029	
	C-N	89.7062	1.2047	
Ferricyanide	Fe ³⁺ -C	8.4069	1.9928	
	C-N	96.6837	1.1933	
Cobalticyanide	Co ³⁺ -C	8.8578	1.9566	
	C-N	97.1404	1.1905	
Three-Body Potentials				
		k [eV]	θ_0 [°]	n
Ferrocyanide	Fe ²⁺ -C-N	0.6451	180	2
	C-Fe ²⁺ -C	0.2352	90	4
Ferricyanide	Fe ³⁺ -C-N	0.5229	180	2
	C-Fe ³⁺ -C	0.1839	90	4
Cobalticyanide	Co ³⁺ -C-N	0.5452	180	2
	C-Co ³⁺ -C	0.2274	90	4
Lennard-Jones Potentials				
		ϵ_{ij} [eV]	r_{ij}^* [Å]	
Ferrocyanide	K	0.02428	3.1229	
	Cl	0.00292	5.2249	
	Fe ²⁺	0.01348	3.6769	
	C	0.00209	3.9559	
Ferricyanide	N	0.00211	3.8072	
	Fe ³⁺	0.01755	3.3708	
	C	0.00235	3.8983	
Cobalticyanide	N	0.00211	3.8072	
	Co ³⁺	0.01810	3.3460	
	C	0.00237	3.8947	
	N	0.00211	3.8072	
Charges				
		ϵ_{ij} [eV]		
Ferrocyanide	K	1.0000		
	Cl _{core}	1.4850		
	Cl _{shell}	-2.4850		
	Fe ²⁺	0.9938		
Ferricyanide	C	-0.2697		
	N	-0.5626		
	Fe ³⁺	1.0549		
Cobalticyanide	C	-0.1297		
	N	-0.5461		
	Co ³⁺	0.9999		
	C	-0.1214		
	N	-0.5453		
Shell Model				
		k [eV Å ⁻²]		
	Cl	29.38		

a potential energy hypersurface was constructed with the density functional techniques built into the DMol^[16] program using the DNP basis set^[17] and BLYP functional.^[18,19] Two- and three-body potential functions describing all the internal degrees of freedom for each complex were fitted to the relevant hypersurface using the GULP code.^[14] The two body interactions were described using a harmonic potential, Equation (2)

$$E_{ij} = \frac{1}{2}k(r_{ij} - r_0)^2 \quad (2)$$

where k is the spring constant, r_0 is the equilibrium bond length, and r_{ij} is the actual length. A cosine potential function was utilized to describe the three body interactions, Equation (3)

$$E_{ijk} = k(-\cos(n\theta_{ijk}) + 1) \quad (3)$$

where k is the three body constant, θ_{ijk} is the bond angle, and n is the periodicity.

The van der Waals parameters for the atoms in the complex as well as the K⁺ and Cl⁻ ions were taken from the ESFF force field,^[20] using the Lennard-Jones 9-6 potential described below, Equation (4)

$$E_{ij} = \epsilon_{ij} \left[2 \left(\frac{r_{ij}^*}{r_{ij}} \right)^9 - 3 \left(\frac{r_{ij}^*}{r_{ij}} \right)^6 \right] \quad (4)$$

where ϵ_{ij} is the potential well depth and r_{ij}^* is the interatomic distance at which the maximum occurs.

Polarization of the chlorine ions was incorporated via the shell model of Catlow et al.^[21] In this model, a massless shell is connected via a spring to the core. The total charge is distributed across the core and shell, thus polarization occurs when they separate. The spring is harmonic, Equation (5)

$$E_i = \frac{1}{2}kr_i^2 \quad (5)$$

where r_i is the core-shell separation. These parameters are summarized in Table 4.

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