

Crystal structures of [18]aneN₆H₂K[Co(CN)₆].4H₂O, [16]aneN₄H₂K[Co(CN)₆] and [12]aneN₄H₃[Co(CN)₆].2H₂O. Insight into the electrostatic and hydrogen-bonding interaction in self-assembling supercomplexes

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Abstract

The crystal structures of [18]aneN₆H₂K[Co(CN)₆].4H₂O [potassium dihydrogen hexacyanocobaltate-1,4,7,10,13,16-hexaazacyclooctadecane-water (1/1/4)], [16]aneN₄H₂K[Co(CN)₆] [potassium dihydrogen hexacyanocobaltate-1,5,9,13-tetraazacyclohexadecane (1/1)] and [12]aneN₄H₃[Co(CN)₆].2H₂O [trihydrogen hexacyanocobaltate-1,4,7,10-tetraazacyclododecane-water (1/1/2)] have been determined. For these supercomplexes, the [Co(CN)₆]³⁻ binding with protonated polyammonium macrocycles is dominant in the binding competition between K⁺ and [Co(CN)₆]³⁻. It is suggested that the binding of [Co(CN)₆]³⁻ with protonated polyammonium macrocycles is independent of the cavity size of the macrocycle, whereas that of K⁺ is size-match selective. For [18]aneN₆H₂K[Co(CN)₆].4H₂O, the formation of a two-dimensional lamella may be derived from a chain-like arrangement of four-, five- and eight-membered rings in the network through the mutual balance between electrostatic and hydrogen-bonding interactions. [16]aneN₄H₂K[Co(CN)₆] is a novel example demonstrating the anchoring of cobaltcyanide through hydrogen-bonding interactions inside a zeolite-type cavity in the three-dimensional network formed by K⁺ and the macrocycles through Coulombic interactions. Also, a three-dimensional network was formed mainly through hydrogen-bonding interactions between [Co(CN)₆]³⁻, protonated macrocycles and water molecules in [12]aneN₄H₃[Co(CN)₆].2H₂O.

1. Introduction

Molecular self-assembly processes designed for the spontaneous generation of one-, two- and three-dimensional solid-state networks incorporating hydrogen bonding (MacDonald & Whitesides, 1994; Endo *et al.*, 1995) and metal-ligand interactions (Guerriero *et al.*, 1995) have been investigated extensively in recent years (Lindsey, 1991; Whitesides *et al.*, 1991; Beer, 1996). Both covalent linkages and noncovalent interactions have been utilized in the self-assembling of network structures (Lawrence *et al.*, 1995). The principal

goal in the synthesis of these materials is to develop strategies for the architecture of components capable of being consolidated into extended structures forming cavities or channels of different sizes that are suitable for specific applications. The binding of metal cyanide anions by polyammonium macrocyclic cations has been an area of continued interest because supercomplexes formed from their interactions have been shown to have significantly different photochemical properties compared with the free anion (Manfrin *et al.*, 1984, 1985; Balzani & Sabbatini, 1986). An analysis based on space-filling models suggested (Manfrin *et al.*, 1985) that encapsulation through hydrogen bonding of cyano groups by the polyammonium macrocyclic receptors in the adduct formed by [Co(CN)₆]³⁻ and polyammonium macrocyclic cations is responsible for the observed moderation of the photochemical quantum yield. Although it has been demonstrated that metal cyanide encapsulation into the macrocyclic ring cavity does not occur in the binding of [Co(CN)₆]³⁻ with the macrocycle [30]aneN₁₀ (Bencini *et al.* 1987), other encapsulating models and their ring-size selectivity remain uncertain. The primary motivation of the study reported here was to synthesize a Prussian-blue-type oriented-network material by utilization of the binding ability of the cyano group with polyammonium macrocyclic cations and to determine their role in the self-assembly processes involving K⁺ and [Co(CN)₆]³⁻. For this purpose, two series of macrocycles were chosen for this study, namely, [32]aneN₈, [24]aneN₆ and [16]aneN₄, and [24]aneN₈, [18]aneN₆ and [12]aneN₄. However, only the supercomplexes formed from cobaltcyanide and [18]aneN₆, [16]aneN₄ and [12]aneN₄ produced crystals of suitable quality for X-ray structure analysis.

2. Experimental

2.1. Materials

[18]aneN₆, [16]aneN₄ and [12]aneN₄ (Fig. 1) were synthesized following literature procedures (Dietrich *et al.*, 1983). Reagent-grade potassium hexacyanocobaltate

Table 1. *Experimental details*

	(1)	(2)	(3)
Crystal data			
Chemical formula	KH ₂ [Co(CN) ₆].C ₁₂ H ₃₀ N ₆ .4H ₂ O	KH ₂ [Co(CN) ₆].C ₁₂ H ₂₈ N ₄	H ₃ [Co(CN) ₆].C ₈ H ₂₀ N ₄ .2H ₂ O
Chemical formula weight	586.65	484.55	426.37
Cell setting	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P1$
a (Å)	10.125 (3)	10.675 (2)	7.635 (2)
b (Å)	11.133 (2)	10.516 (2)	8.202 (5)
c (Å)	15.014 (2)	21.051 (4)	9.442 (3)
α (°)	73.78 (1)	90	109.08 (1)
β (°)	71.68 (1)	91.89 (3)	103.46 (1)
γ (°)	68.87 (2)	90	107.03 (1)
V (Å ³)	1472.0 (6)	2361.9 (8)	497.7 (4)
Z	2	4	1
D_x (Mg m ⁻³)	1.324	1.363	1.423
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073	0.71073
No. of reflections for cell parameters	25	25	25
θ range (°)	5–15	5–15	5–15
μ (mm ⁻¹)	0.769	0.928	0.894
Temperature (K)	293 (2)	293 (2)	293 (2)
Crystal form	Plate	Block	Plate
Crystal size (mm)	0.30 × 0.30 × 0.10	0.35 × 0.30 × 0.22	0.30 × 0.30 × 0.08
Crystal colour	Colourless	Yellow	Colourless
Data collection			
Diffractometer	Siemens $P4$	Rigaku AFC-7R	Siemens $P4$
Data collection method	ω scans	ω scans	ω scans
Absorption correction	Empirical	Empirical	Empirical
T_{\min}	0.833	0.942	0.851
T_{\max}	0.946	1.000	1.000
No. of measured reflections	4910	5713	2375
No. of independent reflections	4617	5425	2374
No. of observed reflections	3032	3133	2015
Criterion for observed reflections	$F > 4\sigma(F)$	$F > 4\sigma(F)$	$F > 4\sigma(F)$
R_{int}	0.0340	0.0211	0.1870
θ_{\max} (°)	24	27.5	27.5
Range of h, k, l	0 → h → 11 -11 → k → 12 -16 → l → 17	0 → h → 13 0 → k → 13 -27 → l → 27	0 → h → 9 -9 → k → 9 -12 → l → 11
No. of standard reflections	3	3	3
Frequency of standard reflections	Every 100 reflections	Every 150 reflections	Every 100 reflections
Intensity decay (%)	1.25	1.72	1.5
Refinement			
Refinement on	F	F	F
R	0.0592	0.0489	0.0614
wR	0.0667	0.0582	0.0741
S	1.38	1.62	1.370
No. of reflections used in refinement	3023	3133	2015
No. of parameters used	325	272	242
H-atom treatment	Riding	Riding	See text
Weighting scheme	$w = 1/[\sigma^2(F_o) + 0.0005F_o^2]$	$w = 1/[\sigma^2(F_o) + 0.0002F_o^2]$	$w = 1/[\sigma^2(F_o) + 0.002(F_o^2)]$
$(\Delta/\sigma)_{\max}$	0.001	0.082	0.15
$\Delta\rho_{\max}$ (e Å ⁻³)	0.360	0.310	0.850
$\Delta\rho_{\min}$ (e Å ⁻³)	-0.620	-0.690	-0.470
Extinction method	None	None	None
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (Vol. C)	<i>International Tables for Crystallography</i> (Vol. C)	<i>International Tables for Crystallography</i> (Vol. C)
Computer programs			
Data collection, cell refinement and data reduction	XSCANS (Siemens, 1994)	MSC/AFC <i>Diffractometer Control Software</i> (Molecular Structure Corporation, 1995)	XSCANS (Siemens, 1994)
Structure solution	SHELXS86 (Sheldrick, 1985)	SHELXS86 (Sheldrick, 1985)	SHELXS86 (Sheldrick, 1985)
Structure refinement	SHELXL93 (Sheldrick, 1993)	SHELXTL/PC (Sheldrick, 1990)	SHELXTL/PC (Sheldrick, 1990)

was purchased from E-Merck and was used without further purification.

2.2. Preparation of crystals

Crystals of $[18]aneN_6H_2K[Co(CN)_6] \cdot 4H_2O$, (1), and $[12]aneN_4H_3[Co(CN)_6] \cdot 2H_2O$, (3), were obtained from mixtures of 5 ml of $10^{-3} M$ $[18]aneN_6$ or $[12]aneN_4$ and equivalent amounts of $10^{-3} M$ $K_3[Co(CN)_6]$ in aqueous solution at room temperature; each solution was adjusted to pH ~ 4 with 1 N HCl. The white precipitate that appeared after addition of ethanol was collected, washed with an H_2O -EtOH (1:1) solvent mixture and dried *in vacuo*. The complexes were redissolved in warm water and then recrystallized by slowly cooling to room temperature. Crystals of $[16]aneN_4H_2K[Co(CN)_6]$, (2), were also obtained from a mixture of 2 ml of $10^{-3} M$ $[16]aneN_4$ and 2 ml of $10^{-3} M$ $K_3[Co(CN)_6]$ in aqueous solution at pH ~ 4 . Single-crystal growth was accomplished by slowly evaporating the solvent in a desiccator over several weeks.

2.3. X-ray crystallography

The details of the data collections and structure refinements for the three complexes are summarized in Table 1. Intensities were collected in the variable ω -scan mode (Sparks, 1976). For each compound, the least-squares refinement of 2θ angles for 25 selected strong reflections produced the crystal class, orientation matrix and unit-cell parameters according to established procedures (Sparks, 1976). The raw data were processed with a learnt procedure (Diamond, 1969) and empirical absorption corrections based on ψ -scan data of selected strong reflections over a range of 2θ angles (Kopfmann & Huber, 1968) were applied.

The crystallographic calculations were performed using the *SHELX* programs (Sheldrick, 1982, 1985, 1990, 1993) on a PC-486 computer. Direct methods yielded the positions of all the non-H atoms and subsequent difference Fourier syntheses were employed to locate the remaining non-H atoms which did not show up in the initial structure. All the non-H atoms were refined anisotropically. H atoms were all generated geometrically (C-H bond lengths fixed at 0.96 Å), assigned appropriate isotropic displacement parameters and allowed to ride on their parent C atoms, with the

exception of one H atom on O2W and the acidic H atoms of the macrocycle in (3), which were not located. All the H atoms were held stationary and included in the structure-factor calculations in the full-matrix least-squares refinement. Analytical expressions for neutral-atom scattering factors were employed, and anomalous-dispersion corrections were incorporated (Ibers & Hamilton, 1974; Hume-Rothery & Lonsdale, 1983).

3. Results and discussion

The final atomic coordinates and equivalent isotropic displacement parameters for the non-H atoms of (1), (2) and (3) are collected in Table 2, while bond lengths and selected bond angles are summarized in Table 3.†

3.1. Ion-binding analysis

Perspective views of the crystal packing of (1), (2) and (3) are shown in Fig. 2. In complex (1), there are two inequivalent protonated $[18]aneN_6$ macrocycles in the unit cell, both of which have inversion centres. It is also demonstrated that one $[18]aneN_6$ is symmetrically capped by two K^+ on either side of the ring plane, while the other $[18]aneN_6$ is bound by two $[Co(CN)_6]^{3-}$ anions, also on either side of the ring plane, with quaternary charged N atoms. Similar to the single-crystal X-ray structure of $[30]aneN_{10}H_8[Co(CN)_6] \cdot Cl_2 \cdot H_2O$ (Bencini *et al.*, 1987), the macrocycles in complexes (2) and (3) are found to be capped unilaterally by $[Co(CN)_6]^{3-}$ anions, with quaternary and doubly charged N atoms, respectively. These results confirm that $[Co(CN)_6]^{3-}$ binding with protonated polyammonium macrocycles through hydrogen bonding and Coulombic interactions is dominant in the binding competition between K^+ and $[Co(CN)_6]^{3-}$ and is independent of the cavity size of the macrocycle. When compared with those in either (1) or (2), the shorter hydrogen-bond distance ($d_{N \dots N} \simeq 2.804\text{--}3.049$ Å) and the reduced cationic character on the N atoms in supercomplex (3) suggest that hydrogen bonding and electrostatic interactions in the second-sphere coordination between $[Co(CN)_6]^{3-}$ and polyammonium macrocycles is mutually complementary. The unique capping of $[18]aneN_6$ by K^+ observed in (1) confirms that metal-ion recognition through the Coulombic interaction is selective and size-matched (Hancock, 1990). As has been demonstrated in metal-ion binding involving 18-crown-6 (Hancock, 1990), K^+ is found to fit well in the $[18]aneN_6$ cavity.

From the views of a part of the crystal packing of each of the three supercomplexes (Fig. 3) and that of $[30]aneN_{10}H_8[Co(CN)_6] \cdot Cl_2 \cdot H_2O$ presented by Bencini *et al.* (1987), there is no experimental evidence

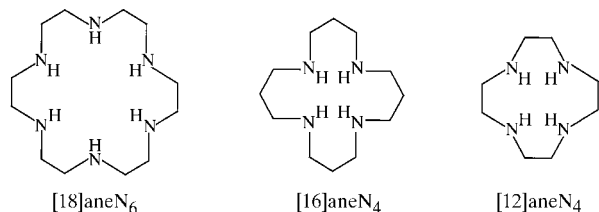


Fig. 1. Schematic diagrams of the polyammonium macrocycles.

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA0016). Services for accessing these data are described at the back of the journal.

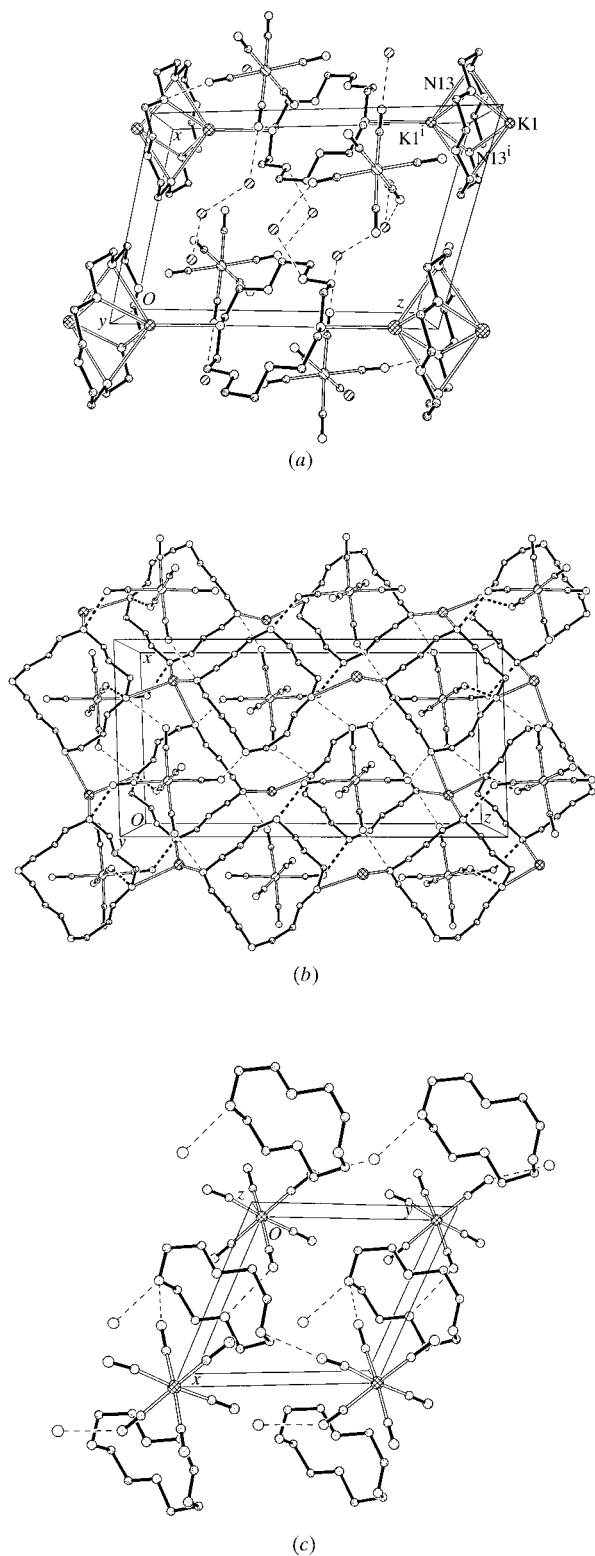


Fig. 2. Perspective drawings of the crystal packing of the supercomplexes (a) [18]aneN₆H₂K[Co(CN)₆].4H₂O [symmetry code: (i) $-x, -y, -z$], (b) [16]aneN₄H₂K[Co(CN)₆] and (c) [12]aneN₄H₃[Co(CN)₆].2H₂O.

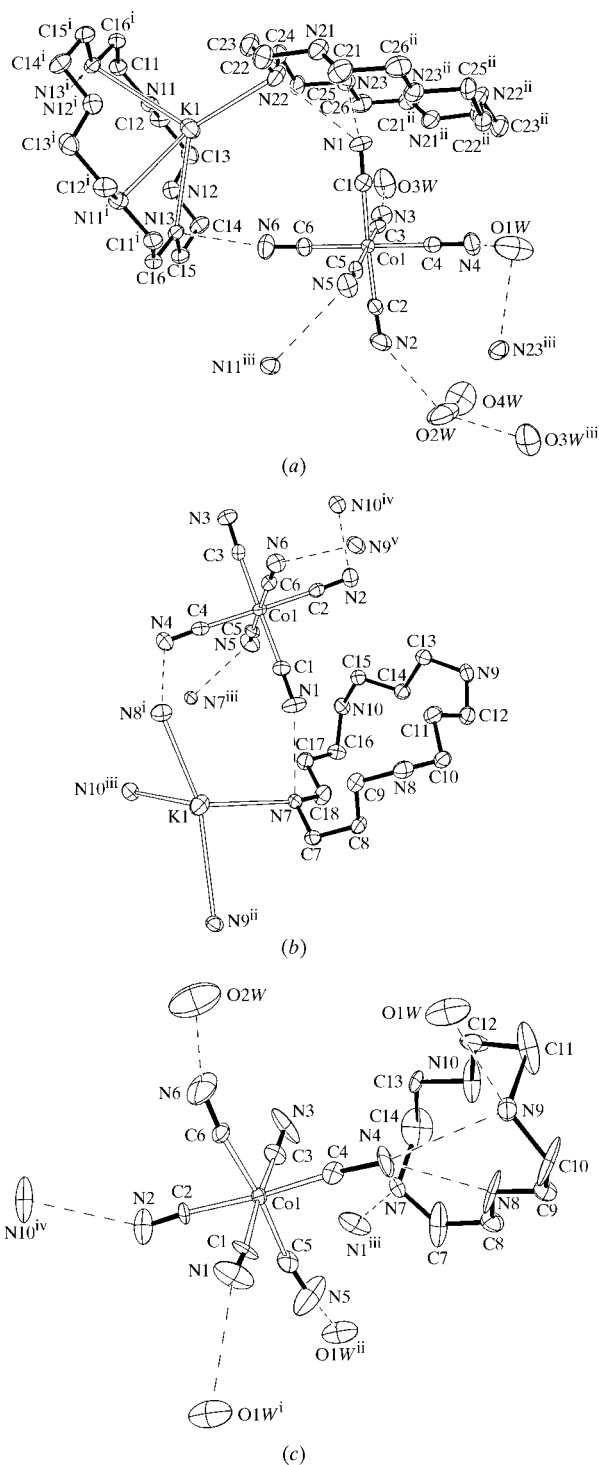


Fig. 3. Perspective drawings (displacement ellipsoids at the 35% probability level) of the crystal structures of supercomplexes (1), (2) and (3). (a) [18]aneN₆H₂K[Co(CN)₆].4H₂O, (1) [symmetry codes: (i) $-x, -y, -z$; (ii) $-x, -y, 1 - z$; (iii) $1 + x, y, z$]. (b) [16]aneN₄H₂K[Co(CN)₆], (2) [symmetry codes: (i) $-x, 1 - y, -z$; (ii) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (iii) $1 - x, 1 - y, -z$; (iv) $1 - x, y + \frac{1}{2}, \frac{1}{2} - z$; (v) $-x, y + \frac{1}{2}, \frac{1}{2} - z$]. (c) [12]aneN₄H₃[Co(CN)₆].2H₂O, (3) [symmetry codes: (i) $x, y, z + 1$; (ii) $x, 1 + y, 1 + z$; (iii) $x, y + 1, z$; (iv) $1 + x, y, 1 + z$].

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

	$U_{\text{eq}} = (1/3)\sum_i \Sigma_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$			
	x	y	z	U_{eq}
Complex (1)				
Co1	0.2607 (1)	0.2764 (1)	0.2894 (1)	0.025 (1)
C1	0.1670 (7)	0.1451 (6)	0.3620 (4)	0.035 (3)
N1	0.1076 (6)	0.0702 (5)	0.4054 (4)	0.048 (3)
C2	0.3494 (7)	0.4107 (6)	0.2223 (4)	0.038 (3)
N2	0.3998 (7)	0.4926 (6)	0.1854 (4)	0.061 (3)
C3	0.0782 (7)	0.4080 (6)	0.3063 (4)	0.036 (3)
N3	-0.0325 (7)	0.4876 (6)	0.3142 (4)	0.054 (3)
C4	0.2940 (7)	0.2896 (6)	0.4040 (5)	0.037 (3)
N4	0.3185 (7)	0.2939 (6)	0.4724 (4)	0.054 (3)
C5	0.4467 (7)	0.1490 (6)	0.2665 (4)	0.035 (3)
N5	0.5575 (6)	0.0730 (6)	0.2514 (4)	0.050 (3)
C6	0.2325 (7)	0.2547 (6)	0.1756 (5)	0.038 (3)
N6	0.2167 (7)	0.2382 (6)	0.1083 (4)	0.061 (3)
K1	-0.0057 (2)	-0.0181 (2)	0.1273 (1)	0.056 (1)
N11	-0.2878 (5)	0.1178 (5)	0.0404 (4)	0.039 (2)
N12	-0.1567 (6)	0.3214 (5)	-0.0442 (4)	0.045 (3)
N13	0.1399 (5)	0.1870 (5)	-0.0389 (3)	0.036 (2)
C11	-0.3514 (7)	0.0193 (6)	0.0349 (5)	0.043 (3)
C12	-0.3747 (7)	0.2553 (6)	0.0151 (5)	0.047 (3)
C13	-0.2992 (8)	0.3453 (7)	0.0214 (5)	0.050 (3)
C14	-0.0642 (7)	0.3888 (6)	-0.0356 (5)	0.048 (3)
C15	0.0901 (8)	0.3273 (6)	-0.0866 (5)	0.046 (3)
C16	0.2899 (7)	0.1173 (6)	-0.0884 (4)	0.041 (3)
N21	0.1576 (6)	-0.3043 (5)	0.4705 (4)	0.050 (3)
N22	-0.0101 (7)	-0.1100 (5)	0.3476 (4)	0.049 (3)
N23	-0.2200 (6)	0.1586 (5)	0.4304 (4)	0.043 (3)
C21	0.2979 (8)	-0.3494 (7)	0.4924 (6)	0.057 (4)
C22	0.1608 (9)	-0.3290 (7)	0.3774 (5)	0.061 (4)
C23	0.0202 (8)	-0.2534 (6)	0.3533 (5)	0.054 (4)
C24	-0.1668 (8)	-0.0391 (7)	0.3622 (5)	0.050 (4)
C25	-0.2009 (9)	0.1085 (7)	0.3438 (5)	0.052 (4)
C26	-0.2851 (8)	0.3060 (7)	0.4179 (5)	0.055 (4)
O1W	0.5410 (6)	0.0953 (7)	0.5561 (4)	0.109 (4)
O2W	0.5361 (7)	0.6723 (7)	0.2006 (5)	0.115 (5)
O3W	-0.3176 (6)	0.6593 (6)	0.3319 (4)	0.097 (4)
O4W	0.3133 (9)	0.9111 (7)	0.2125 (6)	0.142 (6)
Complex (2)				
K1	0.1883 (1)	0.4827 (1)	-0.1228 (1)	0.050 (1)
Co1	0.2773 (1)	0.7967 (1)	0.1154 (1)	0.024 (1)
C1	0.2340 (3)	0.6309 (3)	0.0861 (2)	0.034 (1)
N1	0.2133 (3)	0.5307 (3)	0.0676 (2)	0.054 (1)
C2	0.2784 (3)	0.7396 (3)	0.2007 (2)	0.030 (1)
N2	0.2797 (3)	0.7090 (3)	0.2528 (2)	0.043 (1)
C3	0.3258 (3)	0.9590 (3)	0.1457 (2)	0.031 (1)
N3	0.3537 (3)	1.0568 (3)	0.1662 (2)	0.050 (1)
C4	0.2689 (3)	0.8551 (3)	0.0294 (2)	0.032 (1)
N4	0.2573 (3)	0.8862 (3)	-0.0228 (2)	0.043 (1)
C5	0.4495 (3)	0.7521 (3)	0.1106 (2)	0.032 (1)
N5	0.5526 (3)	0.7239 (3)	0.1106 (2)	0.050 (1)
C6	0.1073 (3)	0.8442 (3)	0.1248 (2)	0.031 (1)
N6	0.0073 (3)	0.8767 (3)	0.1333 (2)	0.039 (1)
N7	0.2863 (3)	0.3083 (3)	-0.0036 (2)	0.031 (1)
N8	-0.0723 (3)	0.2521 (3)	0.1003 (2)	0.039 (1)
N9	0.1996 (3)	0.2945 (3)	0.2989 (2)	0.037 (1)
N10	0.5733 (3)	0.3938 (3)	0.1733 (2)	0.039 (1)
C7	0.1846 (3)	0.2164 (3)	-0.0234 (2)	0.035 (1)
C8	0.0981 (3)	0.1784 (3)	0.0293 (2)	0.034 (1)
C9	0.0189 (3)	0.2885 (3)	0.0505 (2)	0.037 (1)
C10	-0.0193 (3)	0.1949 (3)	0.1598 (2)	0.042 (1)
C11	0.0614 (3)	0.2887 (3)	0.1987 (2)	0.042 (1)
C12	0.1301 (3)	0.2131 (3)	0.2505 (2)	0.042 (1)

Table 2 (cont.)

	x	y	z	U_{eq}
C13	0.2822 (3)	0.3959 (3)	0.2744 (2)	0.037 (1)
C14	0.3870 (3)	0.3410 (3)	0.2350 (2)	0.036 (1)
C15	0.4606 (3)	0.4460 (3)	0.2040 (2)	0.037 (1)
C16	0.5530 (3)	0.2978 (3)	0.1215 (2)	0.039 (1)
C17	0.4772 (3)	0.3494 (3)	0.0643 (2)	0.043 (1)
C18	0.3773 (3)	0.2554 (3)	0.0448 (2)	0.048 (1)
Complex (3)				
Co1	0	0	0	0.019 (1)
C1	-0.1068 (3)	-0.2125 (3)	0.0482 (3)	0.034 (1)
C2	0.2135 (3)	0.1290 (3)	0.2041 (3)	0.031 (1)
C3	0.0837 (3)	0.2040 (3)	-0.0433 (3)	0.032 (1)
C4	-0.1921 (3)	-0.1299 (3)	-0.2050 (3)	0.029 (1)
C5	-0.1527 (3)	0.1068 (3)	0.0987 (3)	0.036 (1)
C6	0.1643 (3)	-0.1085 (3)	-0.0755 (3)	0.033 (1)
N1	-0.1506 (3)	-0.3420 (3)	0.0647 (3)	0.066 (1)
N2	0.3225 (3)	0.1964 (3)	0.3223 (3)	0.057 (1)
N3	0.1400 (3)	0.3316 (3)	-0.0799 (3)	0.071 (1)
N4	-0.3315 (3)	-0.2175 (3)	-0.3367 (3)	0.051 (1)
N5	-0.2505 (3)	0.1810 (3)	0.1454 (3)	0.098 (1)
N6	0.2563 (3)	-0.1745 (3)	-0.1367 (3)	0.090 (1)
N7	-0.2931 (3)	0.2971 (3)	-0.1851 (3)	0.031 (1)
N8	-0.6327 (3)	-0.0621 (3)	-0.4367 (3)	0.073 (1)
N9	-0.5935 (3)	-0.3615 (3)	-0.6614 (3)	0.033 (1)
N10	-0.3752 (3)	0.0608 (3)	-0.5720 (3)	0.062 (1)
C7	-0.4834 (3)	0.2559 (3)	-0.2048 (3)	0.086 (1)
C8	-0.6565 (3)	0.1117 (3)	-0.3447 (3)	0.046 (1)
C9	-0.7954 (3)	-0.2089 (3)	-0.5633 (3)	0.033 (1)
C10	-0.7823 (3)	-0.3874 (3)	-0.6521 (3)	0.073 (1)
C11	-0.5384 (3)	-0.2647 (3)	-0.7836 (3)	0.082 (1)
C12	-0.3536 (3)	-0.0938 (3)	-0.6700 (3)	0.053 (1)
C13	-0.1861 (3)	0.2185 (3)	-0.4356 (3)	0.041 (1)
C14	-0.2347 (3)	0.3568 (3)	-0.3220 (3)	0.091 (1)
O1W	-0.3372 (3)	-0.5152 (3)	-0.7439 (3)	0.072 (1)
O2W	0.2737 (3)	-0.5132 (3)	-0.3581 (3)	0.099 (1)

supporting the encapsulation models proposed earlier (Manfrin *et al.*, 1985). Interestingly, encapsulation of $[\text{PdCl}_4]^{2-}$ by $[\text{30}] \text{aneN}_{10}$ has been demonstrated (Bencini *et al.*, 1990), whereby the backbone of the macrocycle was positioned between two chlorides of $[\text{PdCl}_4]^{2-}$.

3.2. Network-structure analysis

An obvious $A-B-A-B$ {macrocycle capped by two K^+ designated A ; macrocycle capped by two $[\text{Co}(\text{CN})_6]^{3-}$ designated B } one-dimensional chain is observed in complex (1) (Fig. 2a). Apart from capping of $[\text{18}] \text{aneN}_6$, each K^+ interacts further through Coulombic interaction with another $[\text{18}] \text{aneN}_6$ at either N22^{ii} ($\text{K}^+ \cdots \text{N} 3.168 \text{ \AA}$) (Fig. 3a). An entire two-dimensional network is constructed by direct interchain hydrogen bonding occurring at N5 of a cyanide and N11^{iii} (of macrocycle A) from an adjacent chain as well as hydrogen bonding involving water bridges consisting of one $[\text{N4} \cdots \text{O1W} \cdots \text{N23}^{\text{iii}}$ (of macrocycle B)] or two water molecules ($\text{N3} \cdots \text{O3W} \cdots \text{O2W} \cdots \text{N2}$) (Fig. 3a). Note that additional intrachain stabilization may be derived from the arrangement of four-membered ($\text{K1-N13-K1}^{\text{i}}$ -

Table 3. Selected geometric parameters (Å, °)

Complex (1)			
Co1—C1	1.920 (7)	Co1—C2	1.901 (7)
Co1—C3	1.894 (6)	Co1—C4	1.909 (8)
Co1—C5	1.902 (6)	Co1—C6	1.909 (8)
C1—N1	1.137 (9)	C2—N2	1.129 (10)
C3—N3	1.147 (8)	C4—N4	1.146 (11)
C5—N5	1.135 (8)	C6—N6	1.143 (11)
K1···N11	3.205 (6)	K1···N13	3.247 (5)
K1···N22	3.168 (6)	K1···C24	3.369 (7)
K1···K1 ⁱ	3.699 (4)	K1···N11 ⁱ	3.298 (5)
K1···N13 ⁱ	3.393 (7)	N11—C11	1.489 (11)
N11—C12	1.475 (7)	N11···K1 ⁱ	3.298 (5)
N12—C13	1.449 (8)	N12—C14	1.447 (11)
N13—C15	1.496 (7)	N13—C16	1.492 (7)
N13···K1 ⁱ	3.393 (7)	C11—C16 ⁱ	1.514 (8)
C12—C13	1.500 (13)	C14—C15	1.505 (9)
C16—C11 ⁱ	1.514 (8)	N21—C21	1.437 (11)
N21—C22	1.486 (11)	N22—C23	1.496 (9)
N22—C24	1.471 (9)	N23—C25	1.486 (10)
N23—C26	1.513 (8)	C21—C26 ⁱⁱ	1.508 (13)
C22—C23	1.469 (11)	C24—C25	1.513 (10)
C26—C21 ⁱⁱ	1.508 (13)		
C1—Co1—C2	177.3 (3)	C1—Co1—C3	90.1 (3)
C2—Co1—C3	88.4 (3)	C1—Co1—C4	89.1 (3)
C2—Co1—C4	88.8 (3)	C3—Co1—C4	92.3 (3)
C1—Co1—C5	92.2 (3)	C2—Co1—C5	89.4 (3)
C3—Co1—C5	177.3 (2)	C4—Co1—C5	89.2 (3)
C1—Co1—C6	89.6 (3)	C2—Co1—C6	92.6 (3)
C3—Co1—C6	90.0 (3)	C4—Co1—C6	177.3 (2)
C5—Co1—C6	88.5 (3)	Co1—C1—N1	177.9 (5)
Co1—C2—N2	177.4 (6)	Co1—C3—N3	178.1 (7)
Co1—C4—N4	177.5 (5)	Co1—C5—N5	178.9 (6)
Co1—C6—N6	178.2 (6)		
Complex (2)			
K1···N7	3.252 (3)	K1···C7	3.497 (4)
K1···N8 ⁱ	3.095 (3)	K1···N9 ⁱⁱ	3.352 (3)
K1···N10 ⁱⁱⁱ	3.077 (3)	Co1—C1	1.901 (4)
Co1—C2	1.894 (4)	Co1—C3	1.889 (3)
Co1—C4	1.910 (4)	Co1—C5	1.903 (3)
Co1—C6	1.899 (3)	C1—N1	1.142 (5)
C2—N2	1.143 (5)	C3—N3	1.151 (5)
C4—N4	1.150 (5)	C5—N5	1.140 (5)
C6—N6	1.140 (5)	N7—C7	1.502 (5)
N7—C18	1.493 (5)	N8—C9	1.503 (5)
N8—C10	1.486 (5)	N9—C12	1.508 (5)
N9—C13	1.487 (5)	N10—C15	1.490 (5)
N10—C16	1.496 (5)		
C1—Co1—C2	90.6 (2)	C1—Co1—C3	177.9 (1)
C2—Co1—C3	88.4 (2)	C1—Co1—C4	89.2 (2)
C2—Co1—C4	177.7 (1)	C3—Co1—C4	91.9 (2)
C1—Co1—C5	89.0 (1)	C2—Co1—C5	89.8 (2)
C3—Co1—C5	89.2 (1)	C4—Co1—C5	92.6 (2)
C1—Co1—C6	93.0 (1)	C2—Co1—C6	87.7 (2)
C3—Co1—C6	88.8 (1)	C4—Co1—C6	90.0 (2)
C5—Co1—C6	176.8 (2)	Co1—C1—N1	176.9 (3)
Co1—C2—N2	177.9 (3)	Co1—C3—N3	177.6 (4)
Co1—C4—N4	175.9 (3)	Co1—C5—N5	176.9 (4)
Co1—C6—N6	176.2 (4)		
Complex (3)			
Co1—C1	1.942 (3)	Co1—C2	1.919 (2)
Co1—C3	1.822 (3)	Co1—C4	1.857 (2)
Co1—C5	1.889 (3)	Co1—C6	1.879 (3)
C1—N1	1.090 (4)	C2—N2	1.068 (3)

Table 3 (cont.)

C3—N3	1.200 (4)	C4—N4	1.244 (3)
C5—N5	1.169 (4)	C6—N6	1.152 (4)
N7—C7	1.344 (3)	N7—C14	1.632 (4)
N8—C8	1.495 (3)	N8—C9	1.383 (2)
N9—C10	1.423 (3)	N9—C11	1.663 (4)
N10—C12	1.385 (3)	N10—C13	1.539 (2)
C7—C8	1.463 (2)	C9—C10	1.476 (3)
C11—C12	1.503 (2)	C13—C14	1.487 (3)
C1—Co1—C2	91.2 (1)	C1—Co1—C3	175.4 (1)
C2—Co1—C3	90.3 (1)	C1—Co1—C4	89.8 (1)
C2—Co1—C4	175.3 (1)	C3—Co1—C4	89.1 (1)
C1—Co1—C5	87.5 (1)	C2—Co1—C5	89.0 (1)
C3—Co1—C5	88.3 (1)	C4—Co1—C5	95.6 (1)
C1—Co1—C6	88.6 (1)	C2—Co1—C6	85.5 (1)
C3—Co1—C6	95.8 (1)	C4—Co1—C6	89.9 (1)
C5—Co1—C6	173.2 (1)	Co1—C1—N1	169.7 (2)
Co1—C2—N2	174.7 (3)	Co1—C3—N3	176.1 (2)
Co1—C4—N4	175.1 (2)	Co1—C5—N5	171.7 (3)
Co1—C6—N6	172.9 (2)	C7—N7—C14	112.9 (2)
C8—N8—C9	118.1 (2)	C10—N9—C11	115.3 (2)
C12—N10—C13	116.0 (2)	N7—C7—C8	127.9 (2)
N8—C8—C7	115.5 (2)	N8—C9—C10	120.2 (2)
N9—C10—C9	113.0 (2)	N9—C11—C12	101.4 (2)
N10—C12—C11	117.1 (2)	N10—C13—C14	110.3 (2)
N7—C14—C13	114.5 (2)		

Symmetry codes for complex (1): (i) $-x, -y, -z$; (ii) $-x, -y, 1-z$.
Symmetry codes for complex (2): (i) $-x, 1-y, -z$; (ii) $x, \frac{1}{2}-y, z-\frac{1}{2}$;
(iii) $1-x, 1-y, -z$.

N13ⁱ), five-membered (N1—N22—C24—C25—N23) and eight-membered (Co1—C1—N1—N22—K1—N13—N6—C6) rings (Fig. 3a) and that their interconnection through a mutual balance between electrostatic and hydrogen-bonding interactions plays a principal role in the propagation of the chain backbone.

In complex (2), the macrocycle [16]aneN₄ forms a distorted square ring and the backbone of its three-dimensional structure is built up from the strong Coulombic interactions between K⁺ and four N atoms from four different [16]aneN₄ units. In a perspective view down the *b* axis of the three-dimensional network (Fig. 2b), it may be seen that the morphology of the network takes a zeolite-type form. The diameter of the cavity is *ca* 10 Å and is sufficient to accommodate [Co(CN)₆]³⁻.

As shown in Figs. 2(c) and 3(c), the crystal structure of (3), unlike (1) and (2), does not involve the K⁺ cation. The macrocycle [12]aneN₄ has a smaller cavity size (estimated diameter 3.99 Å from N7···N9 = 5.169 Å and N8···N10 = 2.712 Å) and lower symmetry with (N7, N9) and (N8, N10) forming a distorted (flattened) tetrahedron. N1, N2 and N4 in [Co(CN)₆]³⁻ form hydrogen bonds with four N atoms from three independent [12]aneN₄ units, with N4 shared by two hydrogen bonds. An *A-B-A-B* one-dimensional chain is formed by [Co(CN)₆]³⁻ (*A*) and [12]aneN₄ (*B*) through hydrogen-bonding interaction between N4 and N2. The two-dimensional layer is formed from cross-linking *via*

hydrogen-bonding interaction between N1 and N7 from adjacent chains. H₂O molecules provide additional hydrogen-bonding interactions between layers to produce a three-dimensional framework.

3.3. Structure distortion in [Co(CN)₆]³⁻

Deviation of [Co(CN)₆]³⁻ from octahedral symmetry is evident from an inspection of the bond angles and bond lengths in Table 3 for all complexes. These results confirm that the second-sphere interactions between [Co(CN)₆]³⁻ and protonated polyammonium macrocycles are undoubtedly responsible for structure distortion, which would be one possible origin of the change in photochemical properties of these supercomplexes.

4. Conclusions

[Co(CN)₆]³⁻ binding with protonated polyammonium macrocycles through hydrogen bonding and Coulombic interactions is confirmed to be dominant in the binding competition between K⁺ and [Co(CN)₆]³⁻. A reasonable interpretation is that the binding between protonated polyammonium macrocycles and [Co(CN)₆]³⁻ is independent of the cavity size of the macrocycle, whereas binding of K⁺ is size-match selective. It is suggested that the hydrogen bonding and electrostatic interactions in the second-sphere coordination between [Co(CN)₆]³⁻ and polyammonium macrocycles are mutually complementary. Also, the mutual balance between electrostatic interactions and hydrogen bonding is the principal factor contributing to the formation of four-, five- and eight-membered rings found in the two-dimensional lamella network of (1) and the three-dimensional zeolite-type network of (2), whereas the network in (3) is mainly controlled by hydrogen bonds. The results presented here conclusively rule out the possibility of other encapsulating models, proposed by Manfrin *et al.* (1985), for metal cyanide macrocycle systems. Therefore, earlier interpretations (Manfrin *et al.*, 1985) suggesting that modification of the photochemical properties of supercomplexes of cobalticyanide anions stems from encapsulation of some of the CN⁻ ligands upon supercomplex formation are questionable. Further studies on the second-sphere interactions and the origin of the modification of the photochemical properties of these supercomplexes using ⁵⁹Co NMR and density functional theoretical calculations are described elsewhere (Zhou *et al.*, 1999).

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