Anion Co-ordination Chemistry. Crystal Structure of the 'Super Complex:' $[H_8L][Co(CN)_6]_2Cl_2{\cdot}10H_2O$ (L = 1,4,7,10,13,16,19,22,25,28-Deca-azacyclotriacontane)

Antonio Bianchi,[a] Enrique Garcia-España,[b] Stefano Mangani,[c] Mauro Micheloni,[d]* Pierluigi Orioli,[d] and Piero Paoletti[d]*

[a] *ISSEC (CNR), Via F. Guerrazzi 27, I-50132 Firenze, Italy*
[b] *Facultad de Ciencias Quimicas, Valencia, Spain*
[c] *Department of Chemistry, University of Siena, Italy*
[d] *Department of Chemistry, Universita di Firenze, Via Maragliano 75, I-50144 Firenze, Italy*

The title octaprotonated deca-aza-macrocycle (L) binds two hexacyanocobaltate(III) anions forming a 'super complex' whose crystal structure has been determined.

Anion co-ordination chemistry is a rapidly growing field.[1] Polyprotonated, polycharged polyaza-macrocycles are especially suitable for binding inorganic and organic anions.[2,3] When the anionic species investigated are metal complexes like $[M^{n+}(CN)_6]^{(6-n)-}$ (M = Fe^{II}, Fe^{III}, Co^{III}, Ru^{III}, *etc.*) the expression 'super complexes' has been used to describe the second-sphere co-ordination.[4] In order to gain insight into the nature of the interactions between polyammonium macrocyclic receptors and the anionic species $[Co(CN)_6]^{3-}$ we have determined the crystal structure of the title 'super complex.' It is the first crystal structure of this kind of super complex so far reported. Crystals of the title compound, suitable for *X*-ray analysis, were obtained by slow evaporation during 3 months of a solution of 0.15 mol dm^{-3} $NaClO_4$ containing 2×10^{-3}

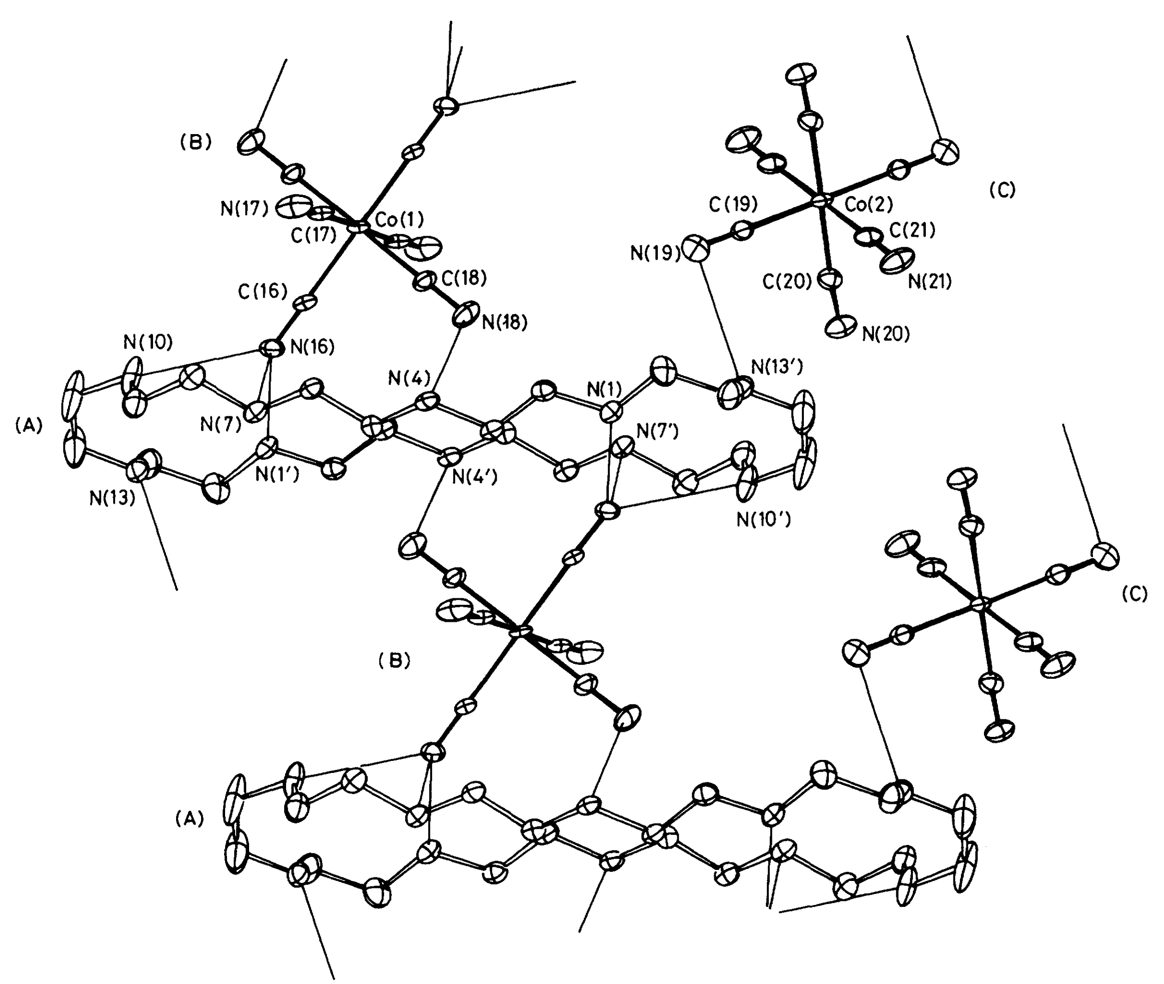

Figure 1. ORTEP[5] view of a portion of the crystal packing showing the 1,4,7,10,13,16,19,22,25,28-deca-azacyclotriacontane ring (A) and the hexacyanocobaltate(III) anions (B) and (C) together with the hydrogen bonds between them. The thermal ellipsoids are drawn at 30% probability.

mol dm^{-3} of $K_3[Co(CN)_6]$ (C. Erba ACS product), purified by double recrystallization from ethanol–water, and 1×10^{-3} mol dm^{-3} of (L)·10HCl·2H_2O (L = 1,4,7,10,13,16,19,22,25,28-deca-azacyclotriacontane).†

The crystal structure of $[H_8L][Co(CN)_6]_2Cl_2 \cdot 10H_2O$ consists of discrete H_8L^{8+} cations (A), $[Co(CN)_6]^{3-}$ anions (B) and (C) which are outside the cavity of the macrocycle (see Figure 1), chloride anions, and water molecules. A difference Fourier map has clearly shown that the atoms N(10) and N(10′) (see Figure 2) are the only two unprotonated nitrogen atoms of the macrocycle. The protonated macrocyclic ligand is centrosymmetric and in the unit cell it is located at 0,0,½. The centrosymmetric hexacyanocobaltate(III) anion (B) lies at 0,0,0, whereas the second, independent, hexacyanocobaltate(III) anion (C) is located on the centre of symmetry at ½,½,½.

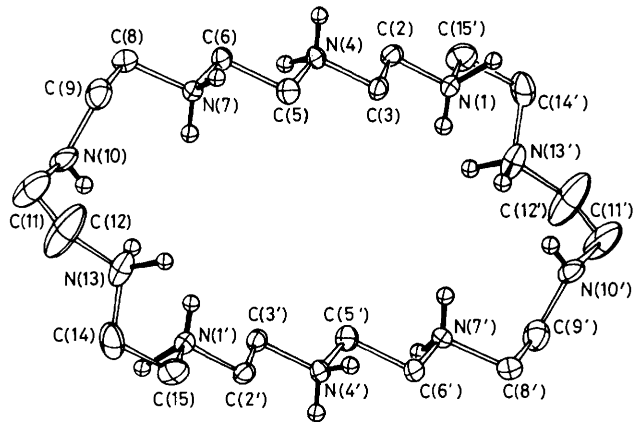

Figure 2. ORTEP[5] drawing of the 1,4,7,10,13,16,19,22,25,28-deca-azacyclotriacontane ring (A) showing the labelling and the hydrogen atoms bonded to the ring nitrogen atoms. The thermal ellipsoids are drawn at 30% probability; the hydrogen atoms are shown as spheres of arbitrary radius.

The macrocycle displays an elongated elliptical shape with the principal axes about 15 and 6 Å long respectively. This particular conformation (see Figure 2) is due to the strong coulombic repulsions between positively charged nitrogens forming two very stiff parallel chains [· · · N(1) · · · N(4) · · ·

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† *Crystal data*: triclinic, space group $P\bar{1}$ (no. 2), $a = 14.818(3)$, $b = 10.414(2)$, $c = 8.974(2)$ Å, $\alpha = 78.68(1)$, $\beta = 85.99(1)$, $\gamma = 89.67(2)°$, $Z = 1$. A total of 4784 reflections ($2\theta \leqslant 50°$, Mo-K_α radiation) were measured on a Philips PW1100 four-circle automatic diffractometer of which 3178 having $I > 3\sigma(I)$ were used in the structure solution and refinement. The structure was solved by the heavy atom technique. Final refinement with anisotropic thermal parameters for all non hydrogen atoms converged at $R = 0.075$ and $R_w = 0.074$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

N(7) · · · and · · · N(1′) · · · N(4′) · · · N(7′) · · ·]. In fact the values of the torsion angles about adjacent bonds in the above chains are all very close to 180°. Six hydrogen bonds, in the range 2.96—3.05 Å, between two cyanide groups belonging to centrosymmetrically related hexacyanocobaltate(III) anions and six nitrogen atoms of the macrocyclic ring (see Figure 1) contribute to stabilizing such a conformation. The macrocyclic nitrogen atoms involved in these hydrogen bonds are N(1), N(7′), N(10′), and N(7), N(10), N(1′). The remaining four nitrogen atoms of the macrocycle are all involved in somewhat weaker bonds with hexacyanocobaltate(III) anions [N(4) · · · N(18) = 3.18 Å and N(13′) · · · N(19) = 3.29 Å]. The hydrogen bonding scheme is completed by several other bonds involving chloride anions and water molecules. Owing to the above hydrogen bonding framework the overall crystal structure shows the presence of parallel polymeric chains · · · (A) · · · (B) · · · (A) · · · (B) · · · crosslinked by weaker hydrogen bonds · · · (C) · · · (A) · · · (C) · · · (A) · · · (see Figure 2).

In conclusion the crystal structure suggests the following: (i) in order for an overall strong interaction to occur it is not necessary for the anionic species to enter the macrocyclic cavity; (ii) potentiometric studies[6] have shown that this interaction is present also in solution, where the rigid conformation of the macrocyclic ring is probably maintained because it is essentially determined by electrostatic repulsions; (iii) both electrostatic interactions and hydrogen bonds between the cationic and anionic species have a synergistic effect in the super complex formation.

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