

# Polymeric potassium diaqua-hexa- $\mu$ -cyano-holmium(III)ruthenium(II) dihydrate

Jason A. Kautz\* and R. Cameron Symes

Department of Chemistry, The University of Texas at Tyler, 3900 University Blvd, Tyler, TX 75799, USA

Correspondence e-mail: jkautz@uttyler.edu

Received 11 December 2002

Accepted 16 June 2003

Online 9 August 2003

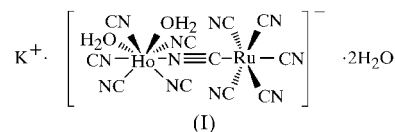
The crystal structure of the title bimetallic cyanide-bridged complex,  $\{K[HoRu(CN)_6(H_2O)_2] \cdot 2H_2O\}_n$ , was determined by means of single-crystal X-ray diffraction techniques. The coordination about the central holmium(III) ion is eightfold in a square-antiprismatic arrangement, while the ruthenium(II) ion is octahedrally coordinated. Channels permeating the crystal lattice contain the potassium cations and two zeolitic water molecules. The  $Ho^{III}$  and K atoms lie at sites with  $mm$  symmetry and the Ru atom is at a site with  $2/m$  symmetry.

## Comment

For over a century, hexacyanometalate ions have been extensively used as building blocks for bridged bimetallic assemblies. The rich chemistry of these prusside-type compounds has led to continued interest in cyanide-bridged lanthanide–transition metal complexes because of their varied uses in an array of practical applications. Mullica *et al.* (1996) demonstrated the structural properties of several early lanthanide double-salt hexacyanoruthenate(II) compounds having the general formula  $LnK[Ru(CN)_6] \cdot 4H_2O$  ( $Ln = La, Ce, Pr$  or  $Nd$ ). These isomorphous complexes crystallize in the hexagonal space group  $P6_3/m$ , with nine-coordinate lanthanide metal centers in a tricapped trigonal-prismatic geometry. Structural data for the title compound, (I), illustrate an eight-coordinate holmium complex that crystallizes in the orthorhombic space group  $Cmcm$ . These results are presented in order to provide a basis for future solid-state chemical studies dealing with the integration and association of diverse cations to applications of semipermeable membranes and the controlled hydration of zeolite-type complexes.

Fig. 1 shows a representation of the polymeric structure of (I). The eight-coordinate holmium(III) ion is located in Wyckoff position  $4c$  ( $0, y, \frac{1}{4}$ ) of the centrosymmetric space group  $Cmcm$  (No. 63), with its ligands arranged in a square-antiprismatic geometry ( $D_{4d}$ ). The holmium(III) metal center is linked to six  $[Ru(CN)_6]^{4-}$  fragments *via* the N atoms of the

cyanide ligands in such a way as to form an infinite three-dimensional polymeric array. The two remaining coordination sites around the Ho atom are occupied by water molecules located *trans* to one another on one of the square faces.



The six-coordinate divalent Ru atoms lie in the  $4b$  ( $0, \frac{1}{2}, \frac{1}{2}$ ) positional site and are covalently bound by the cyano ligands in an octahedral fashion. The two crystallographically unique cyano groups are located in the special site  $8f$  (C1, N1; axial) and the general site  $16h$  (C2, N2; equatorial).

The values of the geometric parameters for (I) (Table 1) are reasonable when considering similar internuclear interactions in other eight-coordinate Ho species (Aslanov *et al.*, 1971; Templeton *et al.*, 1985; Du *et al.*, 2000). The longer of the two Ho–N bonds corresponds to the isocyanide Ho–N1–C1 linkage, bridging to the Ru atom in an axial position, and most likely reflects a steric effect experienced by the bridging unit. The geometric parameters and coordination environment of the Ru atom are consistent with the expected directional (covalent) nature of the bonding of the  $CN^-$  ligands to the Ru metal center. There is little directional influence in the bonding of the  $[Ru(CN)_6]^{4-}$  fragment to the Ho metal center, however, as indicated by the Ho–N–C bond angles of  $167.9$  (3) and  $157.2$  (4) $^\circ$ .

The potassium counter-ions and two uncoordinated zeolitic water molecules are contained in well defined channels that permeate the crystal lattice (Fig. 2). These channels have a pore size of  $5.518$  (1)  $\times$   $5.576$  (1)  $\text{Å}$ , as estimated by calcu-

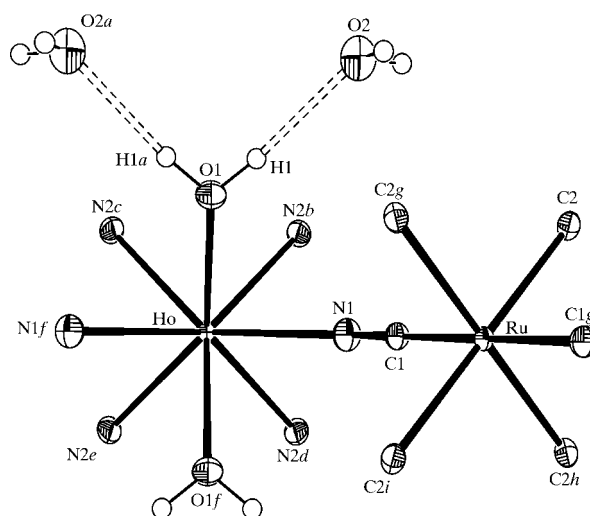
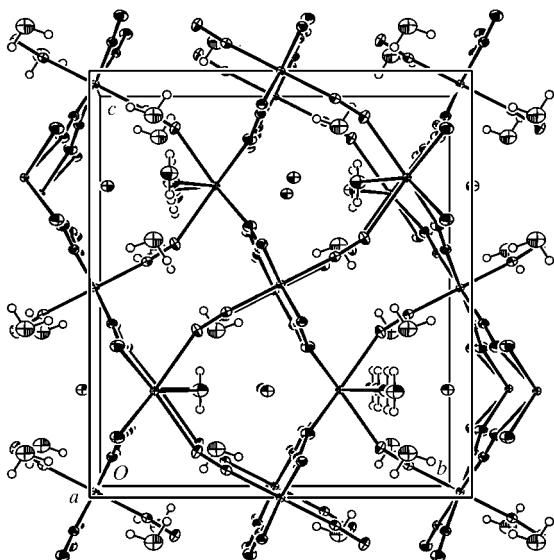


Figure 1

A view of the title compound, showing the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 40% probability level. The  $K^+$  ion has been omitted for clarity. [Symmetry codes: (a)  $x, y, \frac{1}{2} - z$ ; (b)  $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$ ; (c)  $\frac{1}{2} - x, \frac{1}{2} - y, -\frac{1}{2} + z$ ; (d)  $-\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$ ; (e)  $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$ ; (f)  $-x, y, \frac{1}{2} - z$ ; (g)  $x, 1 - y, 1 - z$ ; (h)  $-x, y, z$ ; (i)  $-x, 1 - y, 1 - z$ .]

lating the Ru—C≡N—Ho distances that form the most restrictive channel parameters. The K<sup>+</sup> ions are positioned in the channels so that the centroids of the six closest C≡N groups along with two O atoms (from the coordinated O1 atom) form a square-antiprismatic arrangement around it. The two unique K<sup>+</sup>···CN centroid separations are 2.99 and 2.92 Å for the C1—N1 and C2—N2 groups, respectively. The K<sup>+</sup>···O1 distance is 2.936 (4) Å.



**Figure 2**

A view of the crystal packing along the *a* direction, indicating the location of both the K<sup>+</sup> ions and the uncoordinated water molecules in channels which permeate the lattice.

Intermolecular hydrogen bonding is an important aspect of the molecular structure of (I) (Table 2). An IR study clearly supports two distinct types of water-molecule environment, *viz.* sharp spikes at 3601 and 3527 cm<sup>-1</sup> indicate free O—H stretching, while broad bands over the 3425–3243 cm<sup>-1</sup> region suggest the occurrence of O—H···O hydrogen bonds. The presence of hydrogen bonding is generally accepted if H···O contact distances are appreciably shorter than the van der Waals contact distance between the H and O atoms, and if the appropriate angles are significantly greater than 90°. Based on the maximum of the broad ν(OH) band at 3349 cm<sup>-1</sup>, the empirical rules of Nakamoto *et al.* (1955) predict a corresponding O···O distance of 2.82 Å, which correlates with the O1···O2 distance obtained experimentally. Although the internuclear separations involved in the O2—H2A···N1(½ - *x*, ½ - *y*, 1 - *z*) interaction appear suitable for a weak hydrogen bond, such an interaction is doubtful, especially after careful consideration of geometric constraints. Clearly, the location of atom H2A in the difference Fourier maps indicates that the H-atom orbitals are not in a position that would accommodate an effective overlap with the prospective cyano ligands. In fact, both of the H atoms on atom O2 can be considered free (*i.e.* non-hydrogen bound), conceivably giving rise to the sharp spikes in the ν(OH) region of the IR spectrum.

## Experimental

Single crystals of (I) were prepared by allowing dilute aqueous solutions of K<sub>4</sub>[Ru(CN)<sub>6</sub>] and Ho(NO<sub>3</sub>)<sub>3</sub> polyhydrate to diffuse into one another *via* a glass salt bridge. After six months, pale-purple crystals large enough for single-crystal X-ray analysis were obtained. IR (KBr disc, Mattson–Cygnus 100 FT-IR, cm<sup>-1</sup>): ν(OH)/free water 3601 (*s*), 3527 (*w*); ν(OH)/hydrogen bonding 3349 (*s*, *br*) with shoulders at 3425 (*m*) and 3243 (*m*); ν(CN) 2080 (*vs*), 2047 (*sh*); δ(HOH) 1641 (*m*), 1612 (*m*), 1384 (*w*); δ(RuCN) 567 (*m*), 549 (*m*); ν(RuC) 481 (*m*), 470 (*s*), 462 (*s*), 434 (*m*).

### Crystal data

K[HoRu(CN)<sub>6</sub>(H<sub>2</sub>O)<sub>2</sub>].2H<sub>2</sub>O  
*M<sub>r</sub>* = 533.28  
 Orthorhombic, *Cmcm*  
*a* = 7.4019 (11) Å  
*b* = 12.762 (3) Å  
*c* = 14.2535 (11) Å  
*V* = 1346.4 (4) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 2.631 Mg m<sup>-3</sup>

Mo *K*α radiation  
 Cell parameters from 25 reflections  
 θ = 10–15°  
 μ = 7.28 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Parallelepiped, pale purple  
 0.15 × 0.11 × 0.07 mm

### Data collection

Enraf–Nonius CAD-4 diffractometer  
 ω–2θ scans  
 Absorption correction: numerical (*SHELXTL/PC*; Sheldrick, 1995)  
*T<sub>min</sub>* = 0.397, *T<sub>max</sub>* = 0.608  
 1795 measured reflections  
 1080 independent reflections  
 982 reflections with *I* > 2σ(*I*)

*R<sub>int</sub>* = 0.021  
 θ<sub>max</sub> = 29.9°  
*h* = -2 → 10  
*k* = -2 → 17  
*l* = -2 → 19  
 3 standard reflections  
 frequency: 120 min  
 intensity decay: 3.1%

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.018  
*wR*(*F*<sup>2</sup>) = 0.041  
*S* = 1.11  
 1080 reflections  
 64 parameters  
 H-atom parameters constrained  
*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0119*P*)<sup>2</sup> + 7.6136*P*]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/σ)<sub>max</sub> < 0.001  
 Δρ<sub>max</sub> = 0.73 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -1.03 e Å<sup>-3</sup>  
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.00270 (12)

**Table 1**

Selected geometric parameters (Å, °).

|  |             |  |            |
|--|-------------|--|------------|
| Ho—O1                                  | 2.409 (3)   | C2—N2                                  | 1.161 (4)  |
| Ho—N1                                  | 2.474 (4)   | K <sup>+</sup> ···O1                   | 2.936 (4)  |
| Ho—N2 <sup>i</sup>                     | 2.411 (3)   | K <sup>+</sup> ···C1                   | 2.977 (4)  |
| N1—C1                                  | 1.157 (5)   | K <sup>+</sup> ···N1                   | 3.105 (4)  |
| C1—Ru                                  | 2.034 (4)   | K <sup>+</sup> ···C2 <sup>vi</sup>     | 2.917 (3)  |
| Ru—C2                                  | 2.032 (3)   | K <sup>+</sup> ···N2 <sup>vi</sup>     | 3.038 (3)  |
| O1—Ho—O1 <sup>ii</sup>                 | 102.15 (19) | C1—N1—Ho                               | 157.2 (4)  |
| O1—Ho—N2 <sup>iii</sup>                | 141.61 (6)  | N1—C1—Ru                               | 174.8 (4)  |
| O1—Ho—N2 <sup>iv</sup>                 | 80.11 (10)  | C2 <sup>vi</sup> —Ru—C2                | 180.0      |
| N2 <sup>iii</sup> —Ho—N2 <sup>iv</sup> | 121.70 (13) | C2 <sup>vi</sup> —Ru—C2 <sup>vii</sup> | 90.41 (16) |
| N2 <sup>iii</sup> —Ho—N2 <sup>v</sup>  | 76.78 (13)  | C2—Ru—C2 <sup>vii</sup>                | 89.59 (16) |
| N2 <sup>iv</sup> —Ho—N2 <sup>v</sup>   | 75.77 (13)  | C2 <sup>vi</sup> —Ru—C1 <sup>vi</sup>  | 89.90 (11) |
| O1—Ho—N2 <sup>i</sup>                  | 80.12 (10)  | C2—Ru—C1 <sup>vi</sup>                 | 90.10 (11) |
| O1—Ho—N1                               | 68.86 (7)   | C2—Ru—C1                               | 89.90 (11) |
| N2 <sup>iii</sup> —Ho—N1               | 142.01 (7)  | N2—C2—Ru                               | 175.8 (3)  |
| N2 <sup>iv</sup> —Ho—N1                | 76.77 (10)  | C2—N2—Ho <sup>iv</sup>                 | 167.9 (3)  |

Symmetry codes: (i) ½ - *x*, ½ - *y*, *z* - ½; (ii) -*x*, *y*, ½ - *z*; (iii) *x* - ½, ½ - *y*, *z* - ½; (iv) ½ - *x*, ½ - *y*, 1 - *z*; (v) *x* - ½, ½ - *y*, 1 - *z*; (vi) -*x*, 1 - *y*, 1 - *z*; (vii) *x*, 1 - *y*, 1 - *z*.

**Table 2**

Hydrogen-bonding geometry (Å, °).

| $D-H \cdots A$                   | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|----------------------------------|-------|--------------|--------------|----------------|
| O1–H1 $\cdots$ O2                | 0.83  | 2.02         | 2.821 (4)    | 162            |
| O2–H2A $\cdots$ N1 <sup>iv</sup> | 0.82  | 2.54         | 3.353 (6)    | 171            |

Symmetry code: (iv)  $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$ .

H atoms were placed near appropriate peaks in difference Fourier maps and then constrained to yield reasonable geometry values; isotropic displacement parameters were fixed [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$ ].

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms, 1993); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

The authors thank the University of Texas at Tyler and the Robert A. Welch Foundation for support (grant No. BP-0037),

along with Baylor University, Waco, Texas, for providing the X-ray diffraction facilities.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1406). Services for accessing these data are described at the back of the journal.

## References

- Aslanov, L. A., Korytnyi, E. F. & Porai-Koshits, M. A. (1971). *Zh. Strukt. Khim.* **12**, 661–663.
- Du, B., Meyers, E. A. & Shore, S. G. (2000). *Inorg. Chem.* **39**, 4639–4645.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Harms, K. (1993). *XCAD4*. University of Marburg, Germany.
- Mullica, D. F., Hayward, P. K. & Sappenfield, E. L. (1996). *Inorg. Chim. Acta*, **244**, 273–276.
- Nakamoto, K., Margoshes, M. & Rundle, R. E. (1955). *J. Am. Chem. Soc.* **77**, 6480–6486.
- Sheldrick, G. M. (1995). *SHELXTL/PC*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Templeton, L. K., Templeton, D. H. & Zalkin, A. (1985). *Acta Cryst.* **C41**, 355–358.