Monomers, dimers, and trimers of [Au(CN)]\(_2\)\(^-\) in a Ba(diaza-18-crown-6)\(^{2+}\) coordination polymer

Christine M. Beavers, Latisha Paw U and Marilyn M. Olmstead

*Acta Cryst.* (2009). **E65**, m300–m301

This open-access article is distributed under the terms of the Creative Commons Attribution Licence
http://creativecommons.org/licenses/by/2.0/uk/legalcode, which permits unrestricted use, distribution, and
reproduction in any medium, provided the original authors and source are cited.
Monomers, dimers, and trimers of [Au(CN)₂]⁻ in a Ba(diaza-18-crown-6)²⁺ coordination polymer

Christine M. Beavers, Latisha Paw U and Marilyn M. Olmstead*

Department of Chemistry, University of California, Davis, CA 95656, USA
Correspondence e-mail: mmolmstead@ucdavis.edu
Received 6 February 2009; accepted 13 February 2009

The structure of the title compound, poly[triaquatetra-

Related literature
For aurophilic interactions, see: Anderson et al. (2007); Schmidbaur (1995); Pathaneni & Desiraju (1993). For the structure of a related Pt(CN)₄²⁻ salt, see: Olmstead et al. (2005).
Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2153).

References

Anderson, K. M., Goeta, A. E. & Steed, J. W. (2007). *Inorg. Chem.* 46, 6444–6451.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Olmstead, M. M., Lee, M. A. & Stork, J. R. (2005). *Acta Cryst.* E61, m1048–m1050.
Pathaneni, S. S. & Desiraju, G. R. (1993). *J. Chem. Soc. Dalton Trans.* pp. 319–322.
Schmidbaur, H. (1995). *Chem. Soc. Rev.* 24, 391–400.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A64, 112–122.
supplementary materials
Acta Cryst. (2009). E65, m300-m301  [doi:10.1107/S1600536809005285]

Monomers, dimers, and trimers of [Au(CN)₂]⁻ in a Ba(diaza-18-crown-6)²⁺ coordination polymer

C. M. Beavers, L. Paw U and M. M. Olmstead

Comment

Two coordinate gold(I) compounds often associate through aurophilic interactions that span the range of ca 2.9 - 3.6 Å (Pathaneni & Desiraju, 1993; Schmidbaur, 1995; Anderson et al., 2007). In previous work (Olmstead et al., 2005) we reported a coordination polymer of Ba(18-crown-6)[Pt(CN)₄]₂H₂O. The title compound represents an extension of that work to the [Au(CN)₂]⁻ anion, using a diaza-18-crown-6 to complex Ba²⁺. A related coordination polymer with aurophilic association between gold(I) species is the result.

The asymmetric unit of the title compound consists of two Ba(diaza-18-crown-6)²⁺ cations, four dicyanidoaurate anions, and three molecules of water (Fig. 1). There are five gold positions, two of which, Au2 and Au5, are located on centers of inversion. The monomeric dicyanidoaurate is comprised of Au5, linearly coordinated to two cyanide groups. It functions as a linker anion between two Ba2 complexes via N12 of its cyanide group (Fig. 2). It does not participate in any hydrogen bonding nor aurophilic interactions. The closest dicyanidoaurate is that of Au4, at an Au···Au distance of 4.4501 (2) Å. The Au1 and Au2 atoms are involved in the trimer while Au3 and Au4 form the dimer. Distances and angles are reported in Table 1. As shown in Fig. 2, the polymer is connected through a combination of coordination of the [Au(CN)₂]⁻ nitrogen atoms to barium and aurophilic interactions. All of the hydrogen atoms of the three coordinated waters behave as hydrogen bond donors to N3, N4, N6, N7 and N8 of the cyanide groups (see Table 2). Fig. 3 depicts how a portion of the polymeric structure is supported by these hydrogen bonds.

The bariums, Ba1 and Ba2, have coordination numbers of 9 and 10, respectively. Ba1 is six-coordinated by the diaza-18-crown-6, two [Au(CN)₂]⁻ anions and one water molecule. It is 0.56 (2) Å out of the N₂O₄ plane of the crown, giving endo and exo faces. One dicyanidoaurate is coordinated to each face while the water molecule coordinates on the exo face. The coordination environment of Ba2 is different. Ba2, which is 0.71 (2) Å out of the N₂O₄ plane of the crown, is also coordinated by two dicyanidoaurates, but both are found on the exo face. Two water molecules are coordinated to Ba2, one on each face. Four of the eight independent cyanide groups are coordinated through their cyanide N atom to a barium (N5, N6, N9, N12). Interestingly, even though the dimer and trimer differ in their Au···Au distances, they show similar C-Au-Au-C torsion angles that are intermediate between eclipsed and staggered. The average value of the two smaller angles is 53° for the trimer and 55° for the dimer (see Table 1 for details).

Experimental

A salt of Ba[Au(CN)₂]₂ was prepared by mixing 162 mg (0.62 mmol) Ba(NO₃)₂ and 288 mg (1.0 mmol) K[Au(CN)₂] in water and heating until both compounds were dissolved. The solution was then put in an ice bath to precipitate out Ba[Au(CN)₂]₂. An excess of 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (diaza-18-crown-6), 400 mg (1.5 mmol) was dissolved in methanol and added to the precipitated material. This solution was placed in a 5 mm diameter glass tube and layered with water. After 24 h, suitable prismatic crystals formed.
supplementary materials

Refinement

Hydrogen atoms on water and aza-N atoms were located in a difference map and subsequently refined with $U_{iso} = 1.2U_{eq}(N$ or O) and distance restraints of 0.84 (1) Å for O—H, 0.88 Å for N—H and H···H of 1.32 (3) Å for water. The C—H geometry was determined by a riding model with idealized geometry and a C—H distance of 0.99 Å. The largest difference map peaks are due to a small amount of conformational disorder in one of the aza crown rings but this was not modeled. The disorder is reflected in somewhat elongated thermal ellipsoids in the cation involving Ba2.

Figures

![Fig. 1. A drawing of the asymmetric unit of the title compound. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.](image1)

![Fig. 2. A view that shows how the coordination polymer and the aurophilic interactions are propagated in the title compound. Symmetry codes: (') 2 - x, 1 - y, 2 - z; (") 2 - x, -y, 2 - z; (") x, 1 + y, z.](image2)

![Fig. 3. A portion of the hydrogen bonding that occurs between aqua groups and cyanide groups. Symmetry codes: (") 2 - x, -y, 2 - z; (###) 1 - x, -y, 2 - z; (**) 1 - x, 1 - y, 2 - z.](image3)

poly[tetraquatetra-μ-cyanido-tetracyanidobis(1,4,10,13-tetraoxa-7,16-diazacyclooctadecane)dibarium(II)tetrageold(II)]

Crystal data

$[\text{Au}_4\text{Ba}_2(\text{CN})_8(\text{C}_12\text{H}_{26}\text{N}_2\text{O}_4)_2(\text{H}_2\text{O})_3]$  
$Z = 2$  
$F_{000} = 1700$

Triclinic, $P1$  
$D_x = 2.480 \text{ Mg m}^{-3}$  
Hall symbol: -P 1  
$\lambda = 0.71073 \text{ Å}$

sup-2
supplementary materials

\[ a = 11.0962 \pm 3 \text{ Å} \quad \text{Cell parameters from 7386 reflections} \]
\[ b = 15.9223 \pm 5 \text{ Å} \quad \theta = 2.4-31.5^\circ \]
\[ c = 16.5480 \pm 5 \text{ Å} \quad \mu = 13.43 \text{ mm}^{-1} \]
\[ \alpha = 64.142 \pm 2^\circ \quad T = 90 \text{ K} \]
\[ \beta = 70.523 \pm 2^\circ \quad \text{Prism, colorless} \]
\[ \gamma = 79.027 \pm 3^\circ \quad 0.20 \times 0.15 \times 0.12 \text{ mm} \]
\[ V = 2476.90 \pm 13 \text{ Å}^3 \]

**Data collection**

- **Bruker SMART APEXII**
- **diffractometer**
- **Radiation source**: fine-focus sealed tube
- **Monochromator**: graphite
- **Detector resolution**: 8.3 pixels mm\(^{-1}\)
- **\( T = 90 \text{ K} \)**
- **\( \omega \) scans**
- **Absorption correction**: multi-scan
  (SADABS; Sheldrick, 1996)
- **\( T_{\min} = 0.174, T_{\max} = 0.296 \)**
- **46665 measured reflections**
- **15056 independent reflections**
- **13234 reflections with \( I > 2\sigma(I) \)**
- **\( R_{\text{int}} = 0.028 \)**
- **\( \theta_{\max} = 30.5^\circ \)**
- **\( \theta_{\min} = 2.0^\circ \)**
- **\( h = -15 \rightarrow 15 \)**
- **\( k = -22 \rightarrow 22 \)**
- **\( l = -23 \rightarrow 23 \)**

**Refinement**

- **Refinement on \( F^2 \)**
- **Least-squares matrix**: full
- **\( R[F^2 > 2\sigma(F^2)] = 0.021 \)**
- **\( wR(F^2) = 0.041 \)**
- **\( S = 1.03 \)**
- **15056 reflections**
- **585 parameters**
- **13 restraints**
- **Secondary atom site location: difference Fourier map**
- **Hydrogen site location: inferred from neighbouring sites**
- **H atoms treated by a mixture of independent and constrained refinement**
- **\( w = 1/[(\sigma^2(F_o^2) + (0.01P)^2 + 2.3943P)] \)**
  where \( P = (F_o^2 + 2F_c^2)/3 \)
- **\( (\Delta\sigma)_{\text{max}} = 0.004 \)**
- **\( \Delta\rho_{\text{max}} = 1.06 \text{ e Å}^{-3} \)**
- **\( \Delta\rho_{\text{min}} = -0.89 \text{ e Å}^{-3} \)**
- **Extinction correction: none**

**Special details**

**Geometry.** All e.s.d.’s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.’s are taken into account individually in the estimation of e.s.d.’s in distances, angles and torsion angles; correlations between e.s.d.’s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.’s is used for estimating e.s.d.’s involving l.s. planes.

**Refinement.** Refinement of \( F^2 \) against ALL reflections. The weighted \( R \)-factor \( wR \) and goodness of fit \( S \) are based on \( F^2 \), conventional \( R \)-factors \( R \) are based on \( F \), with \( F \) set to zero for negative \( F^2 \). The threshold expression of \( F^2 > \sigma(F^2) \) is used only for calculating \( R \)-
supplementary materials

factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on $F^2$ are statistically about twice as large as those based on $F$, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\AA^2$)

| Atom | $x$     | $y$     | $z$     | $U_{iso}*/U_{eq}$ |
|------|---------|---------|---------|-------------------|
| Ba1  | 0.755709 (15) | 0.334179 (12) | 0.759393 (11) | 0.01240 (3)      |
| Ba2  | 0.742307 (15) | 0.821847 (11) | 0.765305 (11) | 0.01231 (3)      |
| Au1  | 0.836864 (11) | −0.115019 (9)  | 1.242169 (9)  | 0.02120 (3)      |
| Au2  | 1.0000      | 0.0000      | 1.0000      | 0.01559 (3)      |
| Au3  | 0.551751 (11) | 0.686535 (8)  | 0.561101 (8)  | 0.01723 (3)      |
| Au4  | 0.337214 (11) | 0.634372 (8)  | 0.764727 (8)  | 0.01702 (3)      |
| Au5  | 1.0000      | 0.5000      | 1.0000      | 0.01710 (3)      |
| O1   | 0.8799 (2)  | 0.37038 (15) | 0.56699 (14) | 0.0192 (4)       |
| O2   | 0.49357 (19) | 0.39306 (16) | 0.79701 (15) | 0.0212 (4)       |
| O3   | 0.6317 (2)  | 0.37402 (15) | 0.91746 (15) | 0.0196 (4)       |
| O4   | 1.02624 (19) | 0.34617 (15) | 0.68338 (14) | 0.0178 (4)       |
| O5   | 0.6461 (2)  | 0.17261 (17) | 0.80175 (19) | 0.0304 (6)       |
| H5C  | 0.711 (2)   | 0.141 (2)   | 0.784 (3)   | 0.036*           |
| H5D  | 0.585 (2)   | 0.160 (3)   | 0.791 (3)   | 0.036*           |
| O6   | 0.8761 (3)  | 0.88170 (17) | 0.56832 (16) | 0.0346 (6)       |
| O7   | 0.6071 (3)  | 0.88026 (18) | 0.62624 (19) | 0.0385 (6)       |
| O8   | 0.6167 (2)  | 0.86170 (17) | 0.92912 (16) | 0.0312 (6)       |
| O9   | 0.8862 (3)  | 0.86207 (18) | 0.86293 (18) | 0.0361 (6)       |
| O10  | 0.8497 (2)  | 0.67323 (16) | 0.70570 (17) | 0.0226 (5)       |
| H10C | 0.9171 (19) | 0.644 (2)   | 0.717 (2)   | 0.027*           |
| H10D | 0.803 (3)   | 0.6342 (18) | 0.711 (3)  | 0.027*           |
| O11  | 0.7417 (2)  | 1.01450 (16) | 0.68894 (17) | 0.0241 (5)       |
| H11C | 0.792 (3)   | 1.042 (2)   | 0.696 (2)   | 0.029*           |
| H11D | 0.711 (3)   | 1.0566 (17) | 0.6479 (19) | 0.029*           |
| N1   | 0.6063 (3)  | 0.36039 (19) | 0.63095 (18) | 0.0200 (5)       |
| H1   | 0.597 (4)   | 0.3021 (10) | 0.644 (3)  | 0.032 (11)*      |
| N2   | 0.9045 (2)  | 0.39262 (18) | 0.84017 (18) | 0.0181 (5)       |
| H2   | 0.917 (3)   | 0.4529 (9)  | 0.812 (2)  | 0.030 (10)*      |
| N3   | 0.5818 (3)  | −0.1406 (2) | 1.2162 (2) | 0.0325 (7)       |
| N4   | 1.0905 (3)  | −0.1036 (3) | 1.2788 (2) | 0.0372 (8)       |
| N5   | 0.8290 (2)  | 0.17401 (19) | 0.90908 (18) | 0.0203 (5)       |
| N6   | 0.7368 (3)  | 0.53453 (19) | 0.66500 (19) | 0.0221 (5)       |
| N7   | 0.3765 (3)  | 0.8392 (2)  | 0.4486 (2) | 0.0298 (6)       |
| N8   | 0.1005 (3)  | 0.5907 (2)  | 0.72896 (19) | 0.0249 (6)       |
| N9   | 0.5559 (3)  | 0.68713 (19) | 0.81265 (18) | 0.0216 (5)       |
| N10  | 0.4887 (2)  | 0.9078 (2)  | 0.7923 (2)  | 0.0276 (6)       |
| H10  | 0.508 (3)   | 0.9636 (12) | 0.779 (3)  | 0.033*           |
| N11  | 1.0211 (3)  | 0.8329 (2)  | 0.6984 (2)  | 0.0293 (7)       |
| H11  | 1.036 (4)   | 0.7737 (9)  | 0.712 (3)  | 0.035*           |
| N12  | 0.8064 (3)  | 0.65633 (19) | 0.91243 (18) | 0.0217 (5)       |
| C1   | 0.8104 (3)  | 0.3508 (2)  | 0.5183 (2) | 0.0245 (7)       |
| H11D | 0.8024      | 0.2826      | 0.5430     | 0.029*           |

sup-4
|    |     |     |     |  
|----|-----|-----|-----|----|
| H1B | 0.8566 | 0.3734 | 0.4507 | 0.029* |
| C2  | 0.6811 (3) | 0.3991 (2) | 0.5322 (2) | 0.0250 (7) |
| H1C | 0.6900 | 0.4666 | 0.5112 | 0.030* |
| H2B | 0.6354 | 0.3918 | 0.4936 | 0.030* |
| C3  | 0.4815 (3) | 0.4099 (2) | 0.6491 (2) | 0.0252 (7) |
| H3A | 0.4272 | 0.3997 | 0.6176 | 0.030* |
| H3B | 0.4932 | 0.4778 | 0.6226 | 0.030* |
| C4  | 0.4152 (3) | 0.3767 (2) | 0.7524 (2) | 0.0253 (7) |
| H4A | 0.3309 | 0.4108 | 0.7631 | 0.030* |
| H4B | 0.4009 | 0.3091 | 0.7792 | 0.030* |
| C5  | 0.4311 (3) | 0.3700 (2) | 0.8944 (2) | 0.0259 (7) |
| H5A | 0.4316 | 0.3013 | 0.9295 | 0.031* |
| H5B | 0.3410 | 0.3949 | 0.9032 | 0.031* |
| C6  | 0.5012 (3) | 0.4122 (2) | 0.9303 (2) | 0.0252 (7) |
| H6A | 0.4999 | 0.4810 | 0.8957 | 0.030* |
| H6B | 0.4590 | 0.3976 | 0.9976 | 0.030* |
| C7  | 0.7032 (3) | 0.4129 (2) | 0.9502 (2) | 0.0252 (7) |
| H7A | 0.6608 | 0.4012 | 1.0169 | 0.030* |
| H7B | 0.7071 | 0.4812 | 0.9134 | 0.030* |
| C8  | 0.8359 (3) | 0.3674 (2) | 0.9393 (2) | 0.0231 (7) |
| H8A | 0.8832 | 0.3878 | 0.9683 | 0.028* |
| H8B | 0.8309 | 0.2987 | 0.9719 | 0.028* |
| C9  | 1.0344 (3) | 0.3478 (2) | 0.8259 (2) | 0.0236 (7) |
| H9A | 1.0292 | 0.2790 | 0.8581 | 0.028* |
| H9B | 1.0849 | 0.3674 | 0.8534 | 0.028* |
| C10 | 1.1001 (3) | 0.3746 (2) | 0.7230 (2) | 0.0240 (7) |
| H10A | 1.1085 | 0.4431 | 0.6909 | 0.029* |
| H10B | 1.1870 | 0.3438 | 0.7142 | 0.029* |
| C11 | 1.0825 (3) | 0.3751 (2) | 0.5846 (2) | 0.0243 (7) |
| H11A | 1.1733 | 0.3520 | 0.5717 | 0.029* |
| H11B | 1.0793 | 0.4442 | 0.5535 | 0.029* |
| C12 | 1.0113 (3) | 0.3369 (2) | 0.5466 (2) | 0.0226 (6) |
| H12A | 1.0491 | 0.3576 | 0.4780 | 0.027* |
| H12B | 1.0173 | 0.2678 | 0.5757 | 0.027* |
| C13 | 0.9970 (3) | −0.1053 (2) | 1.2646 (2) | 0.0248 (7) |
| C14 | 0.6740 (3) | −0.1307 (2) | 1.2255 (2) | 0.0243 (7) |
| C15 | 0.8885 (3) | 0.1093 (2) | 0.9446 (2) | 0.0175 (6) |
| C16 | 0.6695 (3) | 0.5908 (2) | 0.6263 (2) | 0.0179 (6) |
| C17 | 0.4399 (3) | 0.7836 (2) | 0.4903 (2) | 0.0217 (6) |
| C18 | 0.1896 (3) | 0.6048 (2) | 0.7407 (2) | 0.0204 (6) |
| C19 | 0.4775 (3) | 0.6657 (2) | 0.7950 (2) | 0.0188 (6) |
| C20 | 0.8099 (5) | 0.8607 (3) | 0.5204 (3) | 0.0476 (12) |
| H20A | 0.7989 | 0.7926 | 0.5479 | 0.057* |
| H20B | 0.8590 | 0.8799 | 0.4535 | 0.057* |
| C21 | 0.6840 (5) | 0.9118 (3) | 0.5291 (3) | 0.0479 (12) |
| H21A | 0.6960 | 0.9796 | 0.5038 | 0.058* |
| H21B | 0.6385 | 0.9021 | 0.4918 | 0.058* |
| C22 | 0.4890 (4) | 0.9331 (3) | 0.6355 (3) | 0.0411 (10) |
| H22A | 0.4389 | 0.9243 | 0.6004 | 0.049* |
supplementary materials

|        | U^{11}      | U^{22}      | U^{33}      | U^{12}      | U^{13}      | U^{23}      |
|--------|-------------|-------------|-------------|-------------|-------------|-------------|
| H22B   | 0.5052      | 1.0003      | 0.6085      | 0.049*      |             |             |
| C23    | 0.4141 (3)  | 0.9032 (3)  | 0.7363 (3)  | 0.0441 (11) |             |             |
| H23A   | 0.3352      | 0.9441      | 0.7419      | 0.053*      |             |             |
| H23B   | 0.3885      | 0.8384      | 0.7609      | 0.053*      |             |             |
| C24    | 0.4193 (4)  | 0.8799 (3)  | 0.8896 (3)  | 0.0449 (11) |             |             |
| H24A   | 0.4107      | 0.8115      | 0.9194      | 0.054*      |             |             |
| H24B   | 0.3324      | 0.9107      | 0.8958      | 0.054*      |             |             |
| C25    | 0.4878 (4)  | 0.9064 (3)  | 0.9372 (3)  | 0.0449 (12) |             |             |
| H25A   | 0.4934      | 0.9752      | 0.9087      | 0.054*      |             |             |
| H25B   | 0.4395      | 0.8873      | 1.0041      | 0.054*      |             |             |
| C26    | 0.6879 (5)  | 0.8926 (3)  | 0.9667 (3)  | 0.0441 (11) |             |             |
| H26A   | 0.6419      | 0.8806      | 1.0329      | 0.053*      |             |             |
| H26B   | 0.6984      | 0.9607      | 0.9314      | 0.053*      |             |             |
| C27    | 0.8161 (4)  | 0.8417 (3)  | 0.9603 (3)  | 0.0430 (11) |             |             |
| H27A   | 0.8651      | 0.8609      | 0.9891      | 0.052*      |             |             |
| H27B   | 0.8053      | 0.7736      | 0.9951      | 0.052*      |             |             |
| C28    | 1.0160 (4)  | 0.8261 (3)  | 0.8502 (3)  | 0.0439 (11) |             |             |
| H28A   | 1.0189      | 0.7569      | 0.8789      | 0.053*      |             |             |
| H28B   | 1.0592      | 0.8475      | 0.8808      | 0.053*      |             |             |
| C29    | 1.0828 (3)  | 0.8602 (3)  | 0.7471 (3)  | 0.0453 (11) |             |             |
| H29A   | 1.0841      | 0.9292      | 0.7200      | 0.054*      |             |             |
| H29B   | 1.1725      | 0.8346      | 0.7378      | 0.054*      |             |             |
| C30    | 1.0738 (4)  | 0.8775 (3)  | 0.5983 (3)  | 0.0507 (13) |             |             |
| H30A   | 1.1665      | 0.8604      | 0.5811      | 0.061*      |             |             |
| H30B   | 1.0632      | 0.9462      | 0.5781      | 0.061*      |             |             |
| C31    | 1.0609      | 0.8766      | 0.4801      | 0.058*      |             |             |
| H31A   | 1.0091 (4)  | 0.8489 (3)  | 0.5484 (3)  | 0.0485 (12) |             |             |
| H31B   | 1.0157      | 0.7801      | 0.5701      | 0.058*      |             |             |
| C32    | 0.8760 (3)  | 0.5980 (2)  | 0.9448 (2)  | 0.0186 (6)  |             |             |

Atomic displacement parameters ($\AA^2$)

|        | U^{11}      | U^{22}      | U^{33}      | U^{12}      | U^{13}      | U^{23}      |
|--------|-------------|-------------|-------------|-------------|-------------|-------------|
| Ba1    | 0.01125 (7) | 0.01328 (8) | 0.01126 (7) | -0.00179 (6) | -0.00387 (6) | -0.00274 (6) |
| Ba2    | 0.01208 (7) | 0.01168 (8) | 0.01154 (7) | -0.00047 (6) | -0.00365 (6) | -0.00308 (6) |
| Au1    | 0.02148 (6) | 0.02113 (6) | 0.02549 (6) | 0.00010 (5)  | -0.00862 (5) | -0.01244 (5) |
| Au2    | 0.01522 (7) | 0.01358 (7) | 0.01744 (7) | 0.00157 (6)  | -0.00750 (6) | -0.00462 (6) |
| Au3    | 0.01753 (5) | 0.01549 (6) | 0.01742 (5) | -0.00105 (4) | -0.00516 (4) | -0.00528 (4) |
| Au4    | 0.01769 (5) | 0.01667 (6) | 0.01733 (5) | -0.00038 (4) | -0.00625 (4) | -0.00666 (4) |
| Au5    | 0.01969 (8) | 0.01373 (8) | 0.01890 (8) | 0.00225 (6)  | -0.01073 (6) | -0.00489 (6) |
| O1     | 0.0210 (11) | 0.0224 (12) | 0.0160 (10) | -0.0025 (9)  | -0.0038 (8)  | -0.0099 (9)  |
| O2     | 0.0146 (10) | 0.0233 (12) | 0.0211 (11) | -0.0044 (9)  | -0.0029 (8)  | -0.0050 (9)  |
| O3     | 0.0197 (11) | 0.0173 (11) | 0.0204 (11) | 0.0014 (8)   | -0.0026 (9)  | -0.0096 (9)  |
| O4     | 0.0138 (10) | 0.0186 (11) | 0.0186 (10) | -0.0028 (8)  | -0.0028 (8)  | -0.0057 (9)  |
| O5     | 0.0321 (14) | 0.0211 (13) | 0.0455 (16) | 0.0010 (11)  | -0.0217 (12) | -0.0133 (12) |
| O6     | 0.0570 (17) | 0.0228 (13) | 0.0167 (12) | -0.0110 (12) | 0.0039 (11)  | -0.0085 (10) |
| O7     | 0.0507 (17) | 0.0250 (14) | 0.0415 (16) | -0.0065 (12) | -0.0318 (14) | 0.0006 (12)  |
| O8     | 0.0482 (16) | 0.0201 (12) | 0.0181 (12) | 0.0000 (11)  | -0.0005 (11) | -0.0083 (10) |
| Code | Value 1  | Value 2  | Value 3  | Value 4  | Value 5  | Value 6  | Value 7  | Value 8  | Value 9  | Value 10 | Value 11 | Value 12 | Value 13 | Value 14 | Value 15 |
|------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| O9   | 0.0453  | 0.0313  | 0.0348  | -0.0091 | -0.0259 | -0.0028 |
| O10  | 0.0205  | 0.0212  | 0.0301  | -0.0005 | -0.0100 | -0.0121 |
| O11  | 0.0274  | 0.0167  | 0.0290  | -0.0023 | -0.0157 | -0.0038 |
| N1   | 0.0242  | 0.0149  | 0.0211  | -0.0020 | -0.0116 | -0.0033 |
| N2   | 0.0242  | 0.0143  | 0.0168  | -0.0027 | -0.0090 | -0.0041 |
| N3   | 0.0294  | 0.0315  | 0.0419  | 0.0025  | -0.0157 | -0.0171 |
| N4   | 0.0334  | 0.053 (2)| 0.0303  | -0.0164 | -0.0080 | -0.0169 |
| N5   | 0.0198  | 0.0196  | 0.0206  | -0.0001 | -0.0064 | -0.0071 |
| N6   | 0.0242  | 0.0173  | 0.0232  | -0.0034 | -0.0046 | -0.0075 |
| N7   | 0.0289  | 0.0247  | 0.0292  | -0.0028 | -0.0103 | -0.0029 |
| N8   | 0.0240  | 0.0292  | 0.0251  | 0.0018  | -0.0080 | -0.0145 |
| N9   | 0.0240  | 0.0176  | 0.0198  | -0.0013 | -0.0081 | -0.0033 |
| N10  | 0.0115  | 0.0229  | 0.0368  | -0.0031 | 0.0001  | -0.0059 |
| N11  | 0.0139  | 0.0155  | 0.0452  | -0.0019 | -0.0018 | -0.0047 |
| N12  | 0.0233  | 0.0185  | 0.0213  | -0.0015 | -0.0060 | -0.0062 |
| C1   | 0.0352  | 0.0253  | 0.0186  | -0.0042 | -0.0113 | -0.0100 |
| C2   | 0.0350  | 0.0220  | 0.0221  | -0.0047 | -0.0163 | -0.0053 |
| C3   | 0.0243  | 0.0192  | 0.0372  | 0.0004  | -0.0207 | -0.0078 |
| C4   | 0.0152  | 0.0203  | 0.040 (2)| 0.0004  | -0.0115 | -0.0100 |
| C5   | 0.0182  | 0.0244  | 0.0198  | -0.0035 | 0.0032  | -0.0006 |
| C6   | 0.0243  | 0.0229  | 0.0210  | 0.0068  | -0.0030 | -0.0079 |
| C7   | 0.0357  | 0.0237  | 0.0198  | -0.0030 | -0.0058 | -0.0128 |
| C8   | 0.0327  | 0.0239  | 0.0176  | -0.0064 | -0.0091 | -0.0094 |
| C9   | 0.0222  | 0.0237  | 0.0256  | -0.0095 | -0.0098 | -0.0049 |
| C10  | 0.0152  | 0.0251  | 0.0313  | -0.0070 | -0.0064 | -0.0087 |
| C11  | 0.0153  | 0.0285  | 0.0197  | -0.0054 | 0.0036  | -0.0058 |
| C12  | 0.0253  | 0.0215  | 0.0177  | 0.0008  | -0.0003 | -0.0099 |
| C13  | 0.0278  | 0.0277  | 0.0198  | -0.0079 | -0.0042 | -0.0096 |
| C14  | 0.0296  | 0.0190  | 0.0306  | 0.0036  | -0.0137 | -0.0139 |
| C15  | 0.0165  | 0.0162  | 0.0181  | -0.0011 | -0.0050 | -0.0052 |
| C16  | 0.0195  | 0.0155  | 0.0189  | -0.0038 | -0.0024 | -0.0081 |
| C17  | 0.0187  | 0.0221  | 0.0202  | -0.0026 | -0.0040 | -0.0054 |
| C18  | 0.0217  | 0.0193  | 0.0214  | 0.0036  | -0.0083 | -0.0095 |
| C19  | 0.0228  | 0.0173  | 0.0136  | -0.0019 | -0.0051 | -0.0035 |
| C20  | 0.095 (4)| 0.029 (2)| 0.0180  | -0.012 (2)| -0.013 (2) | -0.0068 |
| C21  | 0.102 (4)| 0.027 (2)| 0.0231  | -0.023 (2)| -0.035 (2) | 0.0036 |
| C22  | 0.048 (2)| 0.0212  | 0.061 (3)| -0.0042 | -0.041 (2)| -0.0035 |
| C23  | 0.0218  | 0.0214  | 0.096 (4)| 0.0069  | -0.032 (2)| -0.022 (2)|
| C24  | 0.0221  | 0.031 (2)| 0.049 (3)| -0.0013 | 0.0132  | -0.0044 |
| C25  | 0.052 (3)| 0.0237  | 0.0247  | 0.0129  | 0.0159  | -0.0049 |
| C26  | 0.090 (3)| 0.025 (2)| 0.0240  | -0.003 (2)| -0.021 (2)| -0.0123 |
| C27  | 0.085 (3)| 0.029 (2)| 0.0265  | -0.019 (2)| -0.034 (2)| -0.0020 |
| C28  | 0.045 (2)| 0.025 (2)| 0.068 (3)| -0.0060 | -0.042 (2)| -0.004 (2)|
| C29  | 0.0190  | 0.026 (2)| 0.090 (4)| 0.0090  | -0.021 (2)| -0.020 (2)|
| C30  | 0.029 (2)| 0.033 (2)| 0.071 (3)| -0.0104 | 0.023 (2)| -0.027 (2)|
| C31  | 0.057 (3)| 0.029 (2)| 0.035 (2)| -0.0129 | 0.0285  | -0.0169 |
| C32  | 0.0224  | 0.0163  | 0.0167  | -0.0014 | -0.0069 | -0.0051 |
supplementary materials

*Geometric parameters (Å, °)*

| Bond                  | Length (Å) | Angle (°) |
|-----------------------|------------|-----------|
| Ba1—N1                | 2.959 (2)  |           |
| Ba1—N2                | 2.919 (2)  |           |
| Ba1—N5                | 2.889 (3)  |           |
| Ba1—N6                | 2.877 (3)  |           |
| Ba1—O1                | 2.854 (2)  |           |
| Ba1—O2                | 2.827 (2)  |           |
| Ba1—O3                | 2.802 (2)  |           |
| Ba1—O4                | 2.850 (2)  |           |
| Ba1—O5                | 2.764 (2)  |           |
| Ba2—N9                | 2.939 (3)  |           |
| Ba2—N10               | 2.867 (3)  |           |
| Ba2—N11               | 2.929 (3)  |           |
| Ba2—N12               | 2.867 (3)  |           |
| Ba2—O6                | 2.888 (2)  |           |
| Ba2—O7                | 2.884 (2)  |           |
| Ba2—O8                | 2.888 (2)  |           |
| Ba2—O9                | 2.929 (2)  |           |
| Ba2—O10               | 2.859 (2)  |           |
| Ba2—O11               | 2.761 (2)  |           |
| Au1—Au2               | 3.5655 (2) |           |
| Au1—C13               | 1.978 (3)  |           |
| Au1—C14               | 1.991 (3)  |           |
| Au2—C15               | 1.986 (3)  |           |
| Au2—C15               | 1.986 (3)  |           |
| Au3—C16               | 1.985 (3)  |           |
| Au3—C17               | 1.990 (3)  |           |
| Au3—Au4               | 3.2670 (2) |           |
| Au4—C18               | 1.988 (3)  |           |
| Au4—C19               | 1.989 (3)  |           |
| Au5—C32               | 1.985 (3)  |           |
| Au5—C32               | 1.985 (3)  |           |
| O1—C12                | 1.434 (4)  |           |
| O1—C1                 | 1.438 (3)  |           |
| O2—C5                 | 1.432 (4)  |           |
| O2—C4                 | 1.432 (4)  |           |
| O3—C7                 | 1.440 (4)  |           |
| O3—C6                 | 1.443 (4)  |           |
| O4—C11                | 1.431 (4)  |           |
| O4—C10                | 1.437 (3)  |           |
| O5—H5C                | 0.84 (3)   |           |
| O5—H5D                | 0.83 (3)   |           |
| O6—C20                | 1.413 (5)  |           |
| O6—C31                | 1.447 (5)  |           |
| O7—C22                | 1.417 (5)  |           |
| O7—C21                | 1.452 (5)  |           |
| O8—C26                | 1.412 (5)  |           |
|    |    |    |    |
|----|----|----|----|
| O8—C25 | 1.462 (5) | C24—C25 | 1.478 (6) |
| O9—C28 | 1.427 (5) | C24—H24A | 0.9900 |
| O9—C27 | 1.453 (5) | C24—H24B | 0.9900 |
| O10—H10C | 0.83 (4) | C25—H25A | 0.9900 |
| O10—H10D | 0.84 (4) | C25—H25B | 0.9900 |
| O11—H11C | 0.84 (4) | C26—C27 | 1.492 (6) |
| O11—H11D | 0.84 (3) | C26—H26A | 0.9900 |
| N1—C3 | 1.464 (4) | C26—H26B | 0.9900 |
| N1—C2 | 1.467 (4) | C27—H27A | 0.9900 |
| N1—H1 | 0.88 (3) | C27—H27B | 0.9900 |
| N2—C8 | 1.463 (4) | C28—C29 | 1.501 (6) |
| N2—C9 | 1.473 (4) | C28—H28A | 0.9900 |
| N2—H2 | 0.88 (3) | C28—H28B | 0.9900 |
| N3—C14 | 1.134 (4) | C29—H29A | 0.9900 |
| N4—C13 | 1.145 (4) | C29—H29B | 0.9900 |
| N5—C15 | 1.147 (4) | C30—C31 | 1.500 (6) |
| N6—C16 | 1.155 (4) | C30—H30A | 0.9900 |
| N7—C17 | 1.145 (4) | C30—H30B | 0.9900 |
| N8—C18 | 1.147 (4) | C31—H31A | 0.9900 |
| N9—C19 | 1.152 (4) | C31—H31B | 0.9900 |
| N10—C24 | 1.437 (5) |    |    |
| O5—Bal—O3 | 102.83 (7) | O1—C1—H1D | 110.0 |
| O5—Bal—O2 | 79.48 (7) | C2—C1—H1D | 110.0 |
| O3—Bal—O2 | 59.26 (6) | O1—C1—H1B | 110.0 |
| O5—Bal—O4 | 119.33 (7) | C2—C1—H1B | 110.0 |
| O3—Bal—O4 | 119.43 (6) | H1D—C1—H1B | 108.4 |
| O2—Bal—O4 | 159.10 (6) | N1—C2—C1 | 111.0 (3) |
| O5—Bal—O1 | 96.10 (7) | N1—C2—H1C | 109.4 |
| O3—Bal—O1 | 157.80 (6) | C1—C2—H1C | 109.4 |
| O2—Bal—O1 | 114.11 (6) | N1—C2—H2B | 109.4 |
| O4—Bal—O1 | 58.19 (6) | C1—C2—H2B | 109.4 |
| O5—Bal—N6 | 143.22 (7) | H1C—C2—H2B | 108.0 |
| O3—Bal—N6 | 82.11 (7) | N1—C3—C4 | 111.3 (3) |
| O2—Bal—N6 | 71.92 (7) | N1—C3—H3A | 109.4 |
| O4—Bal—N6 | 87.18 (7) | C4—C3—H3A | 109.4 |
| O1—Bal—N6 | 75.77 (7) | N1—C3—H3B | 109.4 |
| O5—Bal—N5 | 66.95 (7) | C4—C3—H3B | 109.4 |
| O3—Bal—N5 | 76.74 (7) | H3A—C3—H3B | 108.0 |
| O2—Bal—N5 | 115.92 (7) | O2—C4—C3 | 108.9 (2) |
| O4—Bal—N5 | 81.94 (7) | O2—C4—H4A | 109.9 |
| O1—Bal—N5 | 122.06 (7) | C3—C4—H4A | 109.9 |
| N6—Bal—N5 | 147.29 (7) | O2—C4—H4B | 109.9 |
| O5—Bal—N2 | 136.59 (7) | C3—C4—H4B | 109.9 |
| O3—Bal—N2 | 60.51 (7) | H4A—C4—H4B | 108.3 |
| O2—Bal—N2 | 114.90 (7) | O2—C5—C6 | 108.6 (3) |
| O4—Bal—N2 | 58.94 (7) | O2—C5—H5A | 110.0 |
| O1—Bal—N2 | 111.94 (7) | C6—C5—H5A | 110.0 |
| N6—Bal—N2 | 77.83 (7) | O2—C5—H5B | 110.0 |
| N5—Bal—N2 | 70.12 (7) | C6—C5—H5B | 110.0 |
| Compound      | Bond Length (Å) | Bond Type        | Bond Length (Å) |
|--------------|----------------|-----------------|----------------|
| O5—Ba1—N1   | 67.30 (7)      | H5A—C5—H5B     | 108.3          |
| O3—Ba1—N1   | 118.09 (7)     | O3—C6—C5       | 108.8 (3)      |
| O2—Ba1—N1   | 58.85 (7)      | O3—C6—H6A      | 109.9          |
| O4—Ba1—N1   | 117.43 (7)     | C5—C6—H6A      | 109.9          |
| O1—Ba1—N1   | 59.24 (7)      | O3—C6—H6B      | 109.9          |
| N6—Ba1—N1   | 78.16 (7)      | C5—C6—H6B      | 109.9          |
| N5—Ba1—N1   | 134.01 (7)     | H6A—C6—H6B     | 108.3          |
| N2—Ba1—N1   | 155.87 (7)     | O3—C7—C8       | 108.5 (2)      |
| O11—Ba2—O10 | 137.70 (7)     | O3—C7—H7A      | 110.0          |
| O11—Ba2—N12 | 143.24 (7)     | C8—C7—H7A      | 110.0          |
| O10—Ba2—N12 | 67.64 (7)      | O3—C7—H7B      | 110.0          |
| O11—Ba2—N10 | 67.46 (8)      | C8—C7—H7B      | 110.0          |
| O10—Ba2—N10 | 131.20 (8)     | H7A—C7—H7B     | 108.4          |
| N12—Ba2—N10 | 120.42 (8)     | N2—C8—C7       | 110.5 (3)      |
| O11—Ba2—O7  | 75.90 (7)      | N2—C8—H8A      | 109.5          |
| O10—Ba2—O7  | 84.97 (7)      | C7—C8—H8A      | 109.5          |
| N12—Ba2—O7  | 140.41 (7)     | N2—C8—H8B      | 109.5          |
| N10—Ba2—O7  | 58.47 (9)      | C7—C8—H8B      | 109.5          |
| O11—Ba2—O8  | 78.61 (7)      | H8A—C8—H8B     | 108.1          |
| O10—Ba2—O8  | 143.09 (7)     | N2—C9—C10      | 110.5 (3)      |
| N12—Ba2—O8  | 77.51 (7)      | N2—C9—H9B      | 109.5          |
| N10—Ba2—O8  | 58.82 (8)      | C10—C9—H9B     | 109.5          |
| O7—Ba2—O8   | 117.22 (8)     | N2—C9—H9C      | 109.5          |
| O11—Ba2—O6  | 72.53 (7)      | C10—C9—H9C     | 109.5          |
| O10—Ba2—O6  | 65.32 (7)      | H9B—C9—H9C     | 108.1          |
| N12—Ba2—O6  | 125.57 (8)     | O4—C10—C9      | 109.3 (2)      |
| N10—Ba2—O6  | 110.74 (8)     | O4—C10—H10A    | 109.8          |
| O7—Ba2—O6   | 58.40 (8)      | C9—C10—H10A    | 109.8          |
| O8—Ba2—O6   | 151.00 (7)     | O4—C10—H10B    | 109.8          |
| O11—Ba2—O9  | 75.86 (7)      | C9—C10—H10B    | 109.8          |
| O10—Ba2—O9  | 115.52 (7)     | H10A—C10—H10B  | 108.3          |
| N12—Ba2—O9  | 67.84 (7)      | O4—C11—C12     | 109.7 (3)      |
| N10—Ba2—O9  | 111.03 (8)     | O4—C11—H11A    | 109.7          |
| O7—Ba2—O9   | 151.71 (7)     | C12—C11—H11A   | 109.7          |
| O8—Ba2—O9   | 58.02 (8)      | O4—C11—H11B    | 109.7          |
| O6—Ba2—O9   | 110.70 (8)     | C12—C11—H11B   | 109.7          |
| O11—Ba2—N11 | 84.00 (7)      | H11A—C11—H11B  | 108.2          |
| O10—Ba2—N11 | 71.79 (7)      | O1—C12—C11     | 108.6 (2)      |
| N12—Ba2—N11 | 81.66 (8)      | O1—C12—H12A    | 110.0          |
| N10—Ba2—N11 | 151.42 (8)     | C11—C12—H12A   | 110.0          |
| O7—Ba2—N11  | 117.33 (9)     | O1—C12—H12B    | 110.0          |
| O8—Ba2—N11  | 115.65 (8)     | C11—C12—H12B   | 110.0          |
| O6—Ba2—N11  | 58.97 (9)      | H12A—C12—H12B  | 108.3          |
| O9—Ba2—N11  | 57.70 (9)      | N4—C13—Au1     | 177.1 (3)      |
| O11—Ba2—N9  | 134.24 (7)     | N3—C14—Au1     | 179.2 (3)      |
| O10—Ba2—N9  | 66.20 (7)      | N5—C15—Au2     | 176.8 (3)      |
| N12—Ba2—N9  | 75.11 (7)      | N6—C16—Au3     | 179.2 (3)      |
| N10—Ba2—N9  | 70.20 (8)      | N7—C17—Au3     | 179.1 (3)      |
| O7—Ba2—N9   | 67.68 (7)      | N8—C18—Au4     | 176.4 (3)      |
| O8—Ba2—N9 | 93.98 (7) | N9—C19—Au4 | 177.2 (3) |
| O6—Ba2—N9 | 108.12 (7) | O6—C20—C21 | 108.0 (3) |
| O9—Ba2—N9 | 137.08 (7) | O6—C20—H20A | 110.1 |
| N11—Ba2—N9 | 137.13 (8) | C21—C20—H20A | 110.1 |
| C13—Au1—C14 | 177.12 (14) | O6—C20—H20B | 110.1 |
| C15ii—Au2—C15 | 179.999 (1) | C21—C20—H20B | 110.1 |
| C16—Au3—C17 | 177.40 (13) | H20A—C20—H20B | 108.4 |
| C16—Au3—Au4 | 87.75 (9) | O7—C21—C20 | 111.0 (3) |
| C17—Au3—Au4 | 94.85 (9) | O7—C21—H21A | 109.4 |
| C18—Au4—C19 | 176.60 (12) | C20—C21—H21A | 109.4 |
| C18—Au4—Au3 | 101.99 (9) | O7—C21—H21B | 109.4 |
| C19—Au4—Au3 | 81.12 (8) | C20—C21—H21B | 109.4 |
| C32ii—Au5—C32 | 179.998 (2) | H21A—C21—H21B | 108.0 |
| C12—O1—C1 | 111.8 (2) | O7—C22—C23 | 110.4 (3) |
| C12—O1—Ba1 | 115.33 (16) | O7—C22—H22A | 109.6 |
| C1—O1—Ba1 | 116.57 (18) | C23—C22—H22A | 109.6 |
| C5—O2—C4 | 111.7 (2) | O7—C22—H22B | 109.6 |
| C5—O2—Ba1 | 113.39 (17) | C23—C22—H22B | 109.6 |
| C4—O2—Ba1 | 119.24 (18) | H22A—C22—H22B | 108.1 |
| C7—O3—C6 | 110.9 (2) | N10—C23—C22 | 111.5 (3) |
| C7—O3—Ba1 | 118.93 (17) | N10—C23—H23A | 109.3 |
| C6—O3—Ba1 | 119.53 (17) | C22—C23—H23A | 109.3 |
| C11—O4—C10 | 110.8 (2) | N10—C23—H23B | 109.3 |
| C11—O4—Ba1 | 119.65 (16) | C22—C23—H23B | 109.3 |
| C10—O4—Ba1 | 121.32 (17) | H23A—C23—H23B | 108.0 |
| Ba1—O5—H5C | 101 (3) | N10—C24—C25 | 109.8 (3) |
| Ba1—O5—H5D | 136 (3) | N10—C24—H24A | 109.7 |
| H5C—O5—H5D | 107 (3) | C25—C24—H24A | 109.7 |
| C20—O6—C31 | 111.5 (3) | N10—C24—H24B | 109.7 |
| C20—O6—Ba2 | 111.6 (2) | C25—C24—H24B | 109.7 |
| C31—O6—Ba2 | 114.4 (2) | H24A—C24—H24B | 108.2 |
| C22—O7—C21 | 111.1 (3) | O8—C25—C24 | 110.8 (3) |
| C22—O7—Ba2 | 120.4 (2) | O8—C25—H25A | 109.5 |
| C21—O7—Ba2 | 116.8 (2) | C24—C25—H25A | 109.5 |
| C26—O8—C25 | 111.7 (3) | O8—C25—H25B | 109.5 |
| C26—O8—Ba2 | 120.0 (2) | C24—C25—H25B | 109.5 |
| C25—O8—Ba2 | 117.8 (2) | H25A—C25—H25B | 108.1 |
| C28—O9—C27 | 113.4 (3) | O8—C26—C27 | 109.3 (3) |
| C28—O9—Ba2 | 115.4 (2) | O8—C26—H26A | 109.8 |
| C27—O9—Ba2 | 112.4 (2) | C27—C26—H26A | 109.8 |
| Ba2—O10—H10C | 120 (2) | O8—C26—H26B | 109.8 |
| Ba2—O10—H10D | 121 (2) | C27—C26—H26B | 109.8 |
| H10C—O10—H10D | 106 (3) | H26A—C26—H26B | 108.3 |
| Ba2—O11—H11C | 121 (2) | O9—C27—C26 | 110.1 (3) |
| Ba2—O11—H11D | 134 (2) | O9—C27—H27A | 109.6 |
| H11C—O11—H11D | 104 (3) | C26—C27—H27A | 109.6 |
| C3—N1—C2 | 112.9 (2) | O9—C27—H27B | 109.6 |
| C3—N1—Ba1 | 114.07 (18) | C26—C27—H27B | 109.6 |
### supplementary materials

| Bond | Distance (Å) | Bond | Distance (Å) |
|------|--------------|------|--------------|
| C2—N1—Ba1 | 112.68 (18) | H27A—C27—H27B | 108.2 |
| C3—N1—H1 | 111 (2) | O9—C28—C29 | 108.8 (3) |
| C2—N1—H1 | 105 (2) | O9—C28—H28A | 109.9 |
| Ba1—N1—H1 | 100 (2) | C29—C28—H28A | 109.9 |
| C8—N2—C9 | 112.6 (2) | O9—C28—H28B | 109.9 |
| C8—N2—Ba1 | 107.68 (17) | C29—C28—H28B | 109.9 |
| C9—N2—Ba1 | 109.42 (17) | H28A—C28—H28B | 108.3 |
| C8—N2—H2 | 110 (2) | N11—C29—C28 | 112.2 (3) |
| C9—N2—H2 | 104 (2) | N11—C29—H29A | 109.2 |
| Ba1—N2—H2 | 113 (2) | C28—C29—H29A | 109.2 |
| C15—N5—Ba1 | 158.4 (2) | N11—C29—H29B | 109.2 |
| C16—N6—Ba1 | 137.8 (2) | C28—C29—H29B | 109.2 |
| C19—N9—Ba2 | 149.6 (2) | H29A—C29—H29B | 107.9 |
| C24—N10—C23 | 113.0 (3) | N11—C30—C31 | 111.3 (3) |
| C24—N10—Ba2 | 112.3 (2) | N11—C30—H30A | 109.4 |
| C23—N10—Ba2 | 115.7 (2) | C31—C30—H30A | 109.4 |
| C24—N10—H10 | 100 (3) | N11—C30—H30B | 109.4 |
| C23—N10—H10 | 116 (3) | C31—C30—H30B | 109.4 |
| Ba2—N10—H10 | 98 (3) | H30A—C30—H30B | 108.0 |
| C30—N11—C29 | 111.7 (3) | O6—C31—C30 | 108.3 (3) |
| C30—N11—Ba2 | 115.4 (2) | O6—C31—H31A | 110.0 |
| C29—N11—Ba2 | 118.3 (2) | C30—C31—H31A | 110.0 |
| C30—N11—H11 | 105 (3) | O6—C31—H31B | 110.0 |
| C29—N11—H11 | 110 (3) | C30—C31—H31B | 110.0 |
| Ba2—N11—H11 | 95 (3) | H31A—C31—H31B | 108.4 |
| C32—N12—Ba2 | 153.4 (2) | N12—C32—Au5 | 178.2 (3) |
| O1—C1—C2 | 108.5 (2) | | |
| C14—Au1—Au2—C15 | 53.73 (13) | O3—Ba1—N1—C2 | 141.49 (19) |
| C13—Au1—Au2—C15 | −127.71 (13) | O2—Ba1—N1—C2 | 143.1 (2) |
| C14—Au1—Au2—C15 | −126.27 (13) | O4—Ba1—N1—C2 | −13.3 (2) |
| C13—Au1—Au2—C15 | 52.29 (13) | O1—Ba1—N1—C2 | −13.15 (19) |
| C16—Au3—Au4—C18 | −125.59 (12) | N6—Ba1—N1—C2 | 67.2 (2) |
| C17—Au3—Au4—C18 | 54.37 (13) | N5—Ba1—N1—C2 | −119.6 (2) |
| C16—Au3—Au4—C19 | 55.81 (12) | N2—Ba1—N1—C2 | 61.5 (3) |
| C17—Au3—Au4—C19 | −124.22 (13) | O5—Ba1—N2—C8 | −51.2 (2) |
| O5—Ba1—O1—C12 | −95.75 (19) | O3—Ba1—N2—C8 | 25.70 (18) |
| O3—Ba1—O1—C12 | 115.7 (2) | O2—Ba1—N2—C8 | 50.2 (2) |
| O2—Ba1—O1—C12 | −176.93 (18) | O4—Ba1—N2—C8 | −152.5 (2) |
| O4—Ba1—O1—C12 | 25.14 (18) | O1—Ba1—N2—C8 | −177.53 (18) |
| N6—Ba1—O1—C12 | 120.7 (2) | N6—Ba1—N2—C8 | 113.4 (2) |
| N5—Ba1—O1—C12 | −29.2 (2) | N5—Ba1—N2—C8 | −59.96 (19) |
| N2—Ba1—O1—C12 | 50.4 (2) | N1—Ba1—N2—C8 | 119.2 (2) |
| N1—Ba1—O1—C12 | −154.7 (2) | O5—Ba1—N2—C9 | 71.4 (2) |
| O5—Ba1—O1—C1 | 38.4 (2) | O3—Ba1—N2—C9 | 148.3 (2) |
| O3—Ba1—O1—C1 | −110.1 (2) | O2—Ba1—N2—C9 | 172.83 (17) |
| O2—Ba1—O1—C1 | −42.8 (2) | O4—Ba1—N2—C9 | −29.84 (17) |
| O4—Ba1—O1—C1 | 159.3 (2) | O1—Ba1—N2—C9 | −54.9 (2) |
| N6—Ba1—O1—C1 | −105.1 (2) | N6—Ba1—N2—C9 | −123.9 (2) |
### supplementary materials

| N5—Ba1—O1—C1 | 104.9 (2) | N5—Ba1—N2—C9 | 62.67 (19) |
| N2—Ba1—O1—C1 | -175.44 (19) | N1—Ba1—N2—C9 | -118.2 (2) |
| N1—Ba1—O1—C1 | -20.59 (19) | O5—Ba1—N5—C15 | 92.1 (6) |
| O5—Ba1—O2—C5 | 84.9 (2) | O3—Ba1—N5—C15 | -157.5 (6) |
| O3—Ba1—O2—C5 | -27.02 (19) | O2—Ba1—N5—C15 | 156.8 (6) |
| O4—Ba1—O2—C5 | -119.6 (2) | O4—Ba1—N5—C15 | -34.6 (6) |
| O1—Ba1—O2—C5 | 176.92 (19) | O1—Ba1—N5—C15 | 9.6 (7) |
| N6—Ba1—O2—C5 | -118.5 (2) | N6—Ba1—N5—C15 | -106.4 (6) |
| N5—Ba1—O2—C5 | 27.1 (2) | N2—Ba1—N5—C15 | -94.4 (6) |
| N2—Ba1—O2—C5 | -51.9 (2) | N1—Ba1—N5—C15 | 86.0 (6) |
| N1—Ba1—O2—C5 | 154.6 (2) | O5—Ba1—N6—C16 | 4.4 (4) |
| O5—Ba1—O2—C4 | -49.8 (2) | O3—Ba1—N6—C16 | -96.5 (3) |
| O3—Ba1—O2—C4 | -161.8 (2) | O2—Ba1—N6—C16 | -36.4 (3) |
| O4—Ba1—O2—C4 | 105.7 (2) | O4—Ba1—N6—C16 | 143.2 (3) |
| O1—Ba1—O2—C4 | 42.2 (2) | O1—Ba1—N6—C16 | 85.4 (3) |
| N6—Ba1—O2—C4 | 106.7 (2) | N5—Ba1—N6—C16 | -146.4 (3) |
| N5—Ba1—O2—C4 | -107.6 (2) | N2—Ba1—N6—C16 | -157.9 (4) |
| N2—Ba1—O2—C4 | 173.4 (2) | N1—Ba1—N6—C16 | 24.5 (3) |
| N1—Ba1—O2—C4 | 19.9 (2) | O11—Ba2—N9—C19 | 38.5 (5) |
| O5—Ba1—O3—C7 | 143.6 (2) | O10—Ba2—N9—C19 | -95.8 (5) |
| O2—Ba1—O3—C7 | -147.1 (2) | N12—Ba2—N9—C19 | -167.6 (5) |
| O4—Ba1—O3—C7 | 8.8 (2) | N10—Ba2—N9—C19 | 61.7 (5) |
| O1—Ba1—O3—C7 | -68.5 (3) | O7—Ba2—N9—C19 | -1.4 (5) |
| N6—Ba1—O3—C7 | -73.4 (2) | O8—Ba2—N9—C19 | 116.4 (5) |
| N5—Ba1—O3—C7 | 81.4 (2) | O6—Ba2—N9—C19 | -44.5 (5) |
| N2—Ba1—O3—C7 | 7.0 (2) | O9—Ba2—N9—C19 | 161.6 (4) |
| N1—Ba1—O3—C7 | -145.5 (2) | N11—Ba2—N9—C19 | -108.1 (5) |
| O5—Ba1—O3—C6 | -75.0 (2) | O11—Ba2—N10—C24 | -120.0 (3) |
| O2—Ba1—O3—C6 | -5.7 (2) | O10—Ba2—N10—C24 | 105.5 (3) |
| O4—Ba1—O3—C6 | 150.1 (2) | N12—Ba2—N10—C24 | 19.6 (3) |
| O1—Ba1—O3—C6 | 72.8 (3) | O7—Ba2—N10—C24 | 153.1 (3) |
| N6—Ba1—O3—C6 | 67.9 (2) | O8—Ba2—N10—C24 | -29.9 (2) |
| N5—Ba1—O3—C6 | -137.2 (2) | O6—Ba2—N10—C24 | -179.7 (2) |
| N2—Ba1—O3—C6 | 148.3 (2) | O9—Ba2—N10—C24 | -56.3 (3) |
| N1—Ba1—O3—C6 | -4.1 (2) | N11—Ba2—N10—C24 | -116.9 (3) |
| O5—Ba1—O4—C11 | 85.4 (2) | N9—Ba2—N10—C24 | 77.8 (3) |
| O3—Ba1—O4—C11 | -147.1 (2) | O11—Ba2—N10—C23 | 108.2 (3) |
| O2—Ba1—O4—C11 | -66.7 (3) | O10—Ba2—N10—C23 | -26.3 (3) |
| O1—Ba1—O4—C11 | 7.2 (2) | N12—Ba2—N10—C23 | -112.1 (2) |
| N6—Ba1—O4—C11 | -67.8 (2) | O7—Ba2—N10—C23 | 21.3 (2) |
| N5—Ba1—O4—C11 | 143.2 (2) | O8—Ba2—N10—C23 | -161.7 (3) |
| N2—Ba1—O4—C11 | -145.2 (2) | O6—Ba2—N10—C23 | 48.5 (3) |
| N1—Ba1—O4—C11 | 7.3 (2) | O9—Ba2—N10—C23 | 171.9 (2) |
| O5—Ba1—O4—C10 | -129.2 (2) | N11—Ba2—N10—C23 | 111.3 (3) |
| O3—Ba1—O4—C10 | -1.6 (2) | N9—Ba2—N10—C23 | -54.0 (2) |
| O2—Ba1—O4—C10 | 78.7 (3) | O11—Ba2—N11—C30 | -63.8 (2) |
| O1—Ba1—O4—C10 | 152.7 (2) | O10—Ba2—N11—C30 | 81.0 (2) |
| N6—Ba1—O4—C10 | 77.7 (2) | N12—Ba2—N11—C30 | 150.2 (3) |
| N5—Ba1—O4—C10 | -71.4 (2) | N10—Ba2—N11—C30 | -66.7 (3) |
### supplementary materials

| Bond          | Length (Å) | Bond          | Length (Å) |
|---------------|------------|---------------|------------|
| N2—Ba1—O4—C10| 0.2 (2)    | O7—Ba2—N11—C30| 6.9 (3)    |
| N1—Ba1—O4—C10| 152.8 (2)  | O8—Ba2—N11—C30| –138.1 (2) |
| O11—Ba2—O6—C20| –114.7 (2)| O6—Ba2—N11—C30| 9.4 (2)    |
| O10—Ba2—O6—C20| 69.0 (2)   | O9—Ba2—N11—C30| –140.8 (3) |
| N12—Ba2—O6—C20| 101.5 (2)  | N9—Ba2—N11—C30| 92.8 (3)   |
| N10—Ba2—O6—C20| –58.0 (3)  | O11—Ba2—N11—C29| 72.4 (3)   |
| O7—Ba2—O6—C20| –30.8 (2)  | O10—Ba2—N11—C29| –142.8 (3) |
| O8—Ba2—O6—C20| –120.7 (3) | N12—Ba2—N11—C29| –73.6 (3)  |
| O9—Ba2—O6—C20| 178.4 (2)  | N10—Ba2—N11—C29| 69.5 (3)   |
| N11—Ba2—O6—C20| 151.8 (3)  | O7—Ba2—N11—C29| 143.1 (2)  |
| N9—Ba2—O6—C20| 17.1 (3)   | O8—Ba2—N11—C29| –1.9 (3)   |
| O11—Ba2—O6—C31| 117.5 (2)  | O6—Ba2—N11—C29| 145.6 (3)  |
| O10—Ba2—O6—C31| –58.9 (2)  | O9—Ba2—N11—C29| –4.6 (2)   |
| N12—Ba2—O6—C31| –26.4 (3)  | N9—Ba2—N11—C29| –131.0 (2) |
| N10—Ba2—O6—C31| 174.2 (2)  | O11—Ba2—N12—C32| –83.9 (5)  |
| O7—Ba2—O6—C31| –158.6 (2) | O10—Ba2—N12—C32| 57.8 (5)   |
| O8—Ba2—O6—C31| 111.5 (3)  | N10—Ba2—N12—C32| –176.4 (5) |
| O9—Ba2—O6—C31| 50.6 (2)   | O7—Ba2—N12—C32| 107.6 (5)  |
| N11—Ba2—O6—C31| 24.0 (2)   | O8—Ba2—N12—C32| –134.6 (5) |
| N9—Ba2—O6—C31| –110.7 (2) | O6—Ba2—N12—C32| 26.0 (5)   |
| O11—Ba2—O7—C22| –63.9 (2)  | O9—Ba2—N12—C32| –74.3 (5)  |
| O10—Ba2—O7—C22| 154.2 (2)  | N11—Ba2—N12—C32| –15.8 (5)  |
| N12—Ba2—O7—C22| 109.1 (2)  | N9—Ba2—N12—C32| 127.8 (5)  |
| N10—Ba2—O7—C22| 8.1 (2)    | C12—O1—C1—C2| –172.1 (3) |
| O8—Ba2—O7—C22| 5.2 (3)    | Ba1—O1—C1—C2| 52.2 (3)   |
| O6—Ba2—O7—C22| –141.8 (3) | C3—N1—C2—C1| 176.1 (3)  |
| O9—Ba2—O7—C22| –67.3 (3)  | Ba1—N1—C2—C1| 45.0 (3)   |
| N11—Ba2—O7—C22| –139.3 (2)| O1—C1—C2—N1| –65.0 (3)  |
| N9—Ba2—O7—C22| 87.9 (2)   | C2—N1—C3—C4| –172.5 (3) |
| O11—Ba2—O7—C21| 76.0 (2)   | Ba1—N1—C3—C4| –42.2 (3)  |
| O10—Ba2—O7—C21| –66.0 (2)  | C5—O2—C4—C3| 175.2 (3)  |
| N12—Ba2—O7—C21| –111.1 (2) | Ba1—O2—C4—C3| –49.4 (3)  |
| N10—Ba2—O7—C21| 147.9 (3)  | N1—C3—C4—O2| 59.9 (3)   |
| O8—Ba2—O7—C21| 145.0 (2)  | C4—O2—C5—C6| –165.0 (3) |
| O6—Ba2—O7—C21| –2.0 (2)   | Ba1—O2—C5—C6| 56.8 (3)   |
| O9—Ba2—O7—C21| 72.5 (3)   | C7—O3—C6—C5| 179.6 (3)  |
| N11—Ba2—O7—C21| 0.5 (3)    | Ba1—O3—C6—C5| 35.4 (3)   |
| N9—Ba2—O7—C21| –132.3 (3)| O2—C5—C6—O3| –60.2 (3)  |
| O11—Ba2—O8—C26| –72.1 (2)  | C6—O3—C7—C8| 177.4 (3)  |
| O10—Ba2—O8—C26| 99.1 (3)   | Ba1—O3—C7—C8| –38.2 (3)  |
| N12—Ba2—O8—C26| 79.8 (2)   | C9—N2—C8—C7| –178.6 (3) |
| N10—Ba2—O8—C26| –142.5 (3)| Ba1—N2—C8—C7| –57.9 (3)  |
| O7—Ba2—O8—C26| –139.5 (2) | O3—C7—C8—N2| 65.8 (3)   |
| O6—Ba2—O8—C26| –66.2 (3)  | C8—N2—C9—C10| 179.1 (3)  |
| O9—Ba2—O8—C26| 8.3 (2)    | Ba1—N2—C9—C10| 59.4 (3)   |
| N11—Ba2—O8—C26| 5.5 (3)    | C11—O4—C10—C9| 176.9 (3)  |
| N9—Ba2—O8—C26| 153.6 (2)  | Ba1—O4—C10—C9| 28.7 (3)   |
| O11—Ba2—O8—C25| 69.8 (2)   | N2—C9—C10—O4| –59.1 (3)  |
| O10—Ba2—O8—C25| –119.0 (2)| C10—O4—C11—C12| 174.6 (3) |
supplementary materials

N12—Ba2—O8—C25  -138.3 (2)  Ba1—O4—C11—C12  -36.6 (3)
N10—Ba2—O8—C25  -0.6 (2)  C1—O1—C12—C11  169.5 (3)
O7—Ba2—O8—C25  2.4 (3)  Ba1—O1—C12—C11  -54.2 (3)
O6—Ba2—O8—C25  75.7 (3)  O4—C11—C12—O1  58.7 (3)
O9—Ba2—O8—C25  150.2 (3)  C31—O6—C20—C21  -169.0 (3)
N11—Ba2—O8—C25  147.4 (2)  Ba2—O6—C20—C21  61.6 (3)
N9—Ba2—O8—C25  -64.5 (2)  C22—O7—C21—C20  176.5 (3)
O11—Ba2—O9—C28  -118.5 (2)  Ba2—O7—C21—C20  33.1 (4)
O10—Ba2—O9—C28  18.0 (3)  O6—C20—C21—O7  -63.5 (4)
N12—Ba2—O9—C28  67.5 (2)  C21—O7—C22—C23  -177.0 (3)
N10—Ba2—O9—C28  -177.1 (2)  Ba2—O7—C22—C23  -35.1 (4)
O7—Ba2—O9—C28  156.3 (3)  Ba2—N10—C23—C22  -48.9 (3)
O8—Ba2—O9—C28  -53.7 (2)  O7—C22—C23—N10  54.6 (4)
N11—Ba2—O9—C28  -26.7 (2)  C23—N10—C24—C25  -167.2 (3)
N9—Ba2—O9—C28  99.7 (2)  Ba2—N10—C24—C25  59.7 (3)
O11—Ba2—O9—C27  109.4 (2)  C26—O8—C25—C24  174.7 (3)
O10—Ba2—O9—C27  -114.1 (2)  Ba2—O8—C25—C24  29.8 (4)
N12—Ba2—O9—C27  -64.6 (2)  N10—C24—C25—O8  -59.4 (4)
N10—Ba2—O9—C27  50.8 (2)  C25—O8—C26—C27  177.6 (3)
O7—Ba2—O9—C27  112.9 (3)  Ba2—O8—C26—C27  -38.4 (4)
O8—Ba2—O9—C27  24.1 (2)  C28—O9—C27—C26  172.1 (3)
O6—Ba2—O9—C27  174.2 (2)  Ba2—O9—C27—C26  -54.8 (3)
N11—Ba2—O9—C27  -158.8 (3)  O8—C26—C27—O9  61.8 (4)
N9—Ba2—O9—C27  -32.4 (3)  C27—O9—C28—C29  -173.7 (3)
O5—Ba1—N1—C3  103.9 (2)  Ba2—O9—C28—C29  54.6 (3)
O3—Ba1—N1—C3  11.0 (2)  C30—N11—C29—C28  171.3 (3)
O2—Ba1—N1—C3  12.63 (19)  Ba2—N11—C29—C28  33.6 (4)
O4—Ba1—N1—C3  -143.73 (19)  O9—C28—C29—N11  -58.0 (4)
O1—Ba1—N1—C3  -143.6 (2)  C29—N11—C30—C31  -179.9 (3)
N6—Ba1—N1—C3  -63.3 (2)  Ba2—N11—C30—C31  -40.9 (4)
N5—Ba1—N1—C3  109.9 (2)  C20—O6—C31—C30  177.6 (3)
N2—Ba1—N1—C3  -69.0 (3)  Ba2—O6—C31—C30  -54.6 (4)
O5—Ba1—N1—C2  -125.7 (2)  N11—C30—C31—O6  63.8 (4)

Symmetry codes: (i) -x+2, -y, -z+2; (ii) -x+2, -y+1, -z+2.

Hydrogen-bond geometry (Å, °)

\[
\begin{array}{cccccc}
D—H···A & D—H & H···A & D···A & D—H···A \\
O5—H5C···N4^i & 0.84 (3) & 2.19 (2) & 2.997 (4) & 161 (4) \\
O5—H5D···N3^{iii} & 0.84 (3) & 1.98 (3) & 2.804 (4) & 168 (3) \\
O10—H10C···N8^{iv} & 0.83 (4) & 2.09 (3) & 2.916 (3) & 170 (3) \\
O10—H10D···N6 & 0.84 (4) & 2.35 (2) & 3.132 (3) & 156 (3) \\
O11—H11C···N4^{ii} & 0.84 (4) & 2.01 (3) & 2.845 (4) & 177 (3) \\
O11—H11D···N7^{v} & 0.84 (3) & 2.09 (3) & 2.920 (4) & 176 (4)
\end{array}
\]

Symmetry codes: (i) -x+2, -y, -z+2; (ii) -x+1, -y, -z+2; (iv) x+1, y, z; (ii) -x+2, -y+1, -z+2; (v) -x+1, -y+2, -z+1.

sup-15
supplementary materials

Fig. 3