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Synthesis, Structure, and Magnetic Properties of Three Chiral Sodium-Centered Polynuclear Copper(II) Clusters with L-Alanine

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By controlling the reactant proportion, three sodium-centered polynuclear octahedral copper(II)–amino acid clusters, $[Na\subset\{Cu_6(Ala)_8(H_2O)(ClO_4)\}]\cdot4ClO_4\cdot4H_2O$ (**1**), $Na[Na\subset\{Cu_6(Ala)_8(ClO_4)\}]_2\cdot9ClO_4\cdot8H_2O$ (**2**), and $[Na\subset\{Cu_5(Ala)_6(H_2O)_3\}]_n\cdot5n(ClO_4)\cdot3n(H_2O)$ (**3**) (Ala = L-alanine), were synthesized. The structures were characterized by X-ray structure analysis. The structure of **1** can be described as an octahedron formed with six copper atoms in which four $Cu(Ala)_2$ ligands bridge two axial copper ions and capture one Na^+ in the center of the cage and that of **2** as an octahedral dimer that is linked by two carboxylate oxygen atoms. Complex **3** is a chain composed of incomplete octahedron $[NaCu_5]$ units linked together by two carboxylate oxygen atoms. The magnetic susceptibility measurements indicate that all three clusters are ferromagnetic overall, although the intercluster interactions may be antiferromagnetic.
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Introduction

Chemical biology is a new research frontier in contemporary biology. Many transition-metal ions play important roles in some important biological process, such as molecule recognition and catalysis, hydrolysis, oxygen transportation, nitrogen fixation, and so on.[1,2] Amino acids are important biological ligands, as they are the basic building units of proteins. Research on the coordination of metal–amino acid complexes will throw light on the behavior of the active site of metal enzymes.[3] Amino acids have two or more types of coordination atoms and may coordinate through the carboxylate or amino groups to transition-metal ions. Many simple compounds with amino acids as ligands[4–9] have been reported in the past three decades, yet most of them were mononuclear or chain compounds. Recently polynuclear complexes[10–19] with amino acids as ligands have been an interesting research area. Gao and Zheng pointed out that amino acids are useful ligands in the construction of high-nuclearity lanthanide clusters,[11–13] which could act as model compound for the mimicking of the activation and cleavage of phosphate diester. We have reported a series of heptanuclear trigonal prismatic LnM_6 (M = Ni and Cu) clusters,[15] lanthanide-center octahedral LnM_6 (M = Ni and Co) clusters,[16] and a series of high-nuclear Ln–Cu heteronuclear clusters with amino acids as ligands.[17] We also showed glycine, proline, and threonine were useful ligands in the synthesis of sodium-centered hexanuclear copper clusters.[18]

In this paper, we report three sodium-centered polynuclear copper clusters, $[Na\subset\{Cu_6(Ala)_8(H_2O)(ClO_4)\}]\cdot4ClO_4\cdot4H_2O$ (**1**), $Na[Na\subset\{Cu_6(Ala)_8(ClO_4)\}]_2\cdot9ClO_4\cdot8H_2O$ (**2**), and $[Na\subset\{Cu_5(Ala)_6(H_2O)_3\}]_n\cdot5n(ClO_4)\cdot3n(H_2O)$ (**3**). Similar to the copper clusters with threonine, glycine, or proline as a ligand, the structure of complex **1** can be described as an octahedron in which four $Cu(Ala)_2$ fragments bridge two axial copper ions and a Na^+ ion in the center of the octahedron is captured through electrostatic interactions by eight oxygen atoms from the four $Cu(Ala)_2$ fragments. Complex **2** is a dimer of octahedral clusters joined through two carboxylate oxygen atoms coordinating to two axial copper ions. Different from monomer **1** and dimer **2**, complex **3** is a chain composed of incomplete octahedron $[NaCu_5]$ units linked by two carboxylate oxygen atoms with two axial copper ions.

Results and Discussion

The Structure of Complex 1

The structure of the cation of **1** is shown in Figure 1. Six Cu^{2+} ions form an octahedron and a Na^+ ion is captured in the center. The edge distance (Cu···Cu distance) is 5.00 Å, compared with the edge distance of about 5.25 Å (Ni···Ni distance) in the reported lanthanide-centered octahedral complexes $[LnNi_6AA_{12}]$[14,16] $[LnNi_6L_6]$ (L = 3,7-diazanona-2,7-dien-2,8-dicarboxylato).[20] The Cu···Na distance is about 3.55 Å. There are electrovalent bonds between the Na^+ ion and the surrounding eight oxygen atoms of the

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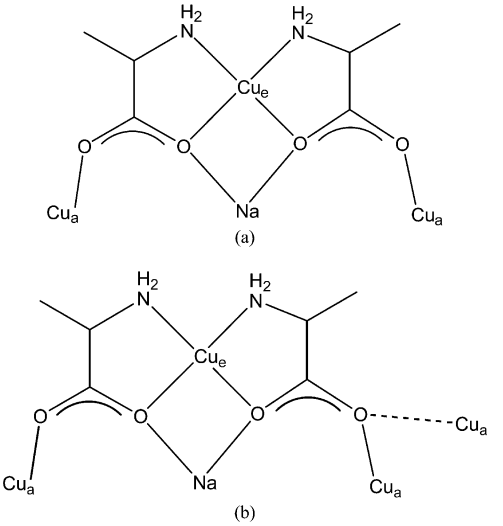
eight amino acids (O1, O3, O5, O7, O9, O11, O13, O15). The average Na–O distance is 2.59 Å. The Cu3, Cu4, Cu5, and Cu6 atoms are all four-coordinate and have quadrangle coordination geometry. Each Cu^{2+} ion coordinates to two L-alanine units through two nitrogen atoms and two oxygen atoms in a *cis*-coordination mode. The average Cu–N distance is about 1.98 Å and the Cu–O distance is about 1.94 Å. The four chelated Cu^{2+} ions are located in the equatorial plane of a regular nonbonding octahedron. In addition, there are one or more weak linkage between the four copper atoms and the neighboring perchlorate ions. The four $CuAla_2$ ligands in the equatorial plane bridge two copper ions (Cu1, Cu2) situated at the axial vertices to construct the framework with the help of Na^+ ions. Each amino acid group acts as a tridentate ligand by utilizing its amino and carboxylate groups to chelate one Cu^{2+} ion and bridge another, as shown in Scheme 1(a). The Cu1 atom has an O_5 donor set, which consists of four oxygen atoms of the carboxylate groups (O2, O6, O10, O14) with an average Cu–O distance of about 1.92 Å and one oxygen atom of water (O17) with the Cu–O distance of about 2.307 Å. The longer distance means weaker coordination. For Cu1, small deviations in the bond angles from the idealized pyramidal geometry are found for the O2–Cu1–O10 [177.5(8)°], O6–Cu1–O14 [179.2(7)°], O17–Cu1–O2 [88.2(7)°], and O17–Cu1–O6 [91.5(6)°] angles, which implies that the Cu^{2+} ion has a slightly distorted pyramidal configuration. The Cu2 atom also has an O_5 donor set and a slightly distorted pyramidal configuration just as that in Cu1, except a ClO_4^- anion is used instead of a water molecule (O17).



Scheme 1. Two coordination modes of the $Cu(Ala)_2$ ligand, which are respectively composed of two alanine ligands with the mode $[3.1_1 2_{23} 1_3]$ (a) and of two alanine ligands with the different modes $[3.1_1 2_{23} 1_3]$ and $[4.2_{12} 2_{34} 1_4]$ (b), indicated by the Harris notation.[21]

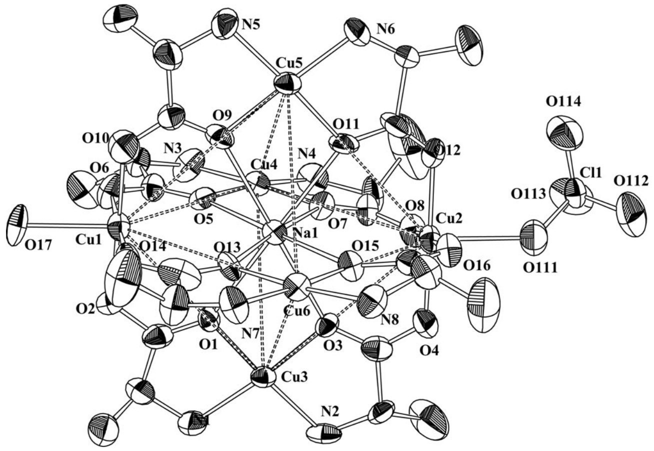


Figure 1. Structure of the cation of **1** (ellipsoids at 30% probability).

The Structure of Complex 2

The structure of the cation of **2** is shown in Figure 2. Complex **2** is the dimer of complex **1**. Eight copper atoms (Cu3–Cu6, Cu9–Cu12) in the equatorial planes are each chelated by two L-alanine units to form the $CuAla_2$ ligand. Their coordination environments are almost the same as that in complex **1**. Four copper atoms (Cu1, Cu2, Cu7, Cu8) at the axial vertices also have O_5 donor sets, which consist of four oxygen atoms of the carboxylate groups and a weak coordinated oxygen atom. The Cu1 and Cu7 atoms are bridged by O18 and O2 of the carboxylate groups to form the dimer. The Cu1–O18 and Cu7–O2 distances are

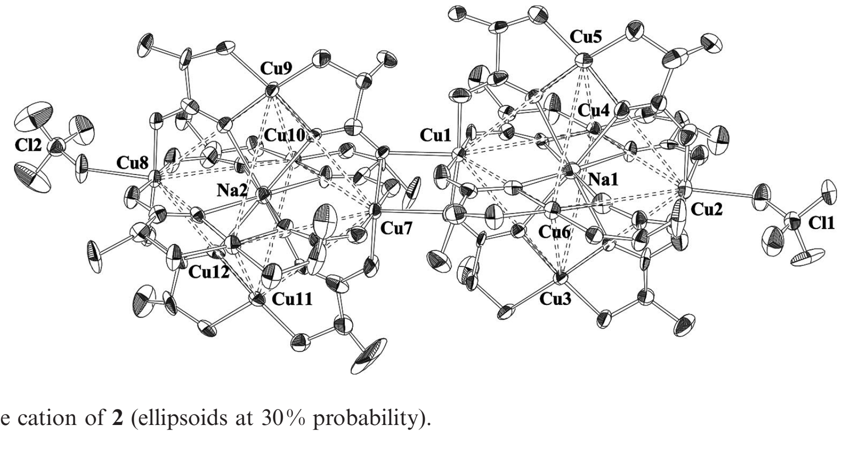


Figure 2. Structure of the cation of **2** (ellipsoids at 30% probability).

2.441(15) and 2.427(16) Å, respectively. The Cu1–O2–Cu7 and Cu1–O18–Cu7 angles are 102.2(6) and 101.4(5)°, respectively. The two L-alanine moieties act as unusual pentadentate ligands by utilizing both their amino and carboxylate groups (Scheme 1b). The Cu1···Cu7 distance is 3.416 Å. The Cu2 and Cu8 atoms are weakly coordinated by the oxygen atom in ClO_4^-, and the Cu2–O111 and Cu8–O121 distances are 2.34(2) and 2.43(2) Å, respectively. The two ClO_4^- ions prevent the $NaCu_6$ basic unit from connecting into a chain structure. A stereoview cation $[Na_2Cu_{12}Ala_{16}(ClO_4)_2]^{8+}$ of complex **2** with the atom-numbering scheme is shown in Figure 2.

The Structure of Complex 3

The structure of the cation of **3** is shown in Figure 3. Complex **3** has a chiral cation chain. Its unit can be viewed as a pyramid consisting of five copper atoms. It also can be viewed as an incomplete octahedron relative to the structure of complex **1**. Three copper atoms chelated by L-alanine moieties (Cu3, Cu4, Cu5) are located in the equatorial plane of an incomplete octahedron (Figure 3). The average Cu_a–Cu_e distance is 5.00 Å and the Cu_e···Cu_e distances Cu4···Cu3 and Cu4···Cu5 are 5.121 and 5.231 Å, respectively. The Cu3–Na1–Cu5 angle is 166.3(1)°. These longer Cu_e–Cu_e distances are caused by the lack of a $CuAla_2$ unit in the equatorial plane. Three water molecules are used to bond Cu1, Cu2, and Na1 in place of the $CuAla_2$ unit. The O2 and O12 atoms are also bonded to the copper Cu1a and Cu2b atoms in another unit with weak coordination just as complex **2** (Figure 4). The Cu1–O12a and Cu2–O2b distances are 2.387(6) and 2.412(6) Å, respectively, and the Cu1–O2–Cu2a and Cu2–O12–Cu1b angles are 102.4(2) and 102.9(3)°, respectively. The Cu1···Cu2b distance is 3.398 Å.

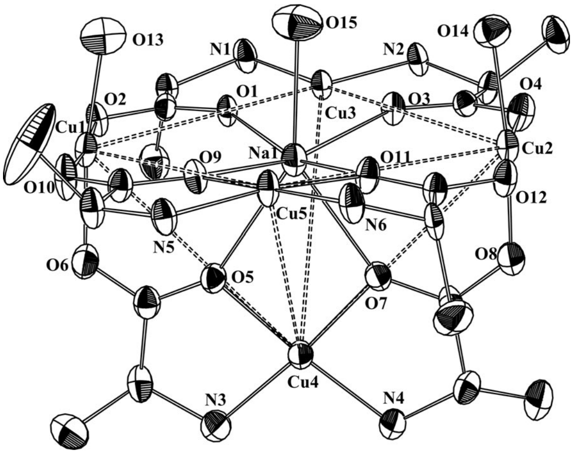


Figure 3. Structure of the cation of **3** (ellipsoids at 30% probability).

The hexanuclear copper(II) complexes were synthesized in an aqueous solution, and the reactant proportion was about 1:1. It is interesting that a small change in the reactant proportion could result in the different structure of the products.

Generally, amino acids have a great ability to coordinate to metal ions to construct coordination architectures. The $M(AA)_2$ (M = transition metal) complexes in which metal ions are chelated by two amino acids have been prepared in several reports.[6] The complexes can be employed as blocks not only for the syntheses of chains or networks,[8c,8d] but also for the preparation of polynuclear clusters such as wheel $[Zn_6Val_{12}]$ (Val = valine)[10] and octahedron $[LnNi_6AA_{12}]$[14,16] and $[NaCu_6(AA)_8]$[18,19] (AA = glycine, alanine, proline, threonine) through the use of the spare carboxylate oxygen atom. In this paper, the $M(AA)_2$ complexes were used as bricks to construct three Na–Cu heterometal clusters. The $Cu(AA)_2$ ligands adopt two coordination fashions, as shown in Scheme 1. One is tridentate to bind two axial copper ions and one Na ion by utilizing their spare carboxylate oxygen atoms. Another is tetradentate, which binds another axial copper ion from an adjacent cluster on the basis of the former mode.

Magnetic Properties

Temperature-dependent magnetization data (bulk magnetization data) were collected from ground crystalline samples of compounds **1**, **2**, and **3** in the temperature range 5–300 K under a constant magnetic field of 10000 G. Plots of the experimental data in the form of $\chi_m T$ vs. T per $[Cu_n]$ (n = 6 for **1** and **2**, n = 5 for **3**) unit, where χ_m is the molar magnetic susceptibility, as calculated without correcting for the diamagnetic contribution of the compounds are displayed in Figure 5. At 300 K, the $\chi_m T$ values per $[Cu_6]$ unit for **1** and **2** are 2.35 and 2.26 $cm^3 K mol^{-1}$, which is close to the value of 2.25 $cm^3 K mol^{-1}$ calculated for six spin-only Cu^{II} ions (S = 1/2, g = 2). Similarly, the $\chi_m T$ value per $[Cu_5]$ unit for **3** is 2.07 $cm^3 K mol^{-1}$, which is close to the value of 1.88 $cm^3 K mol^{-1}$ for five spin-only Cu^{II} ions. With a de-

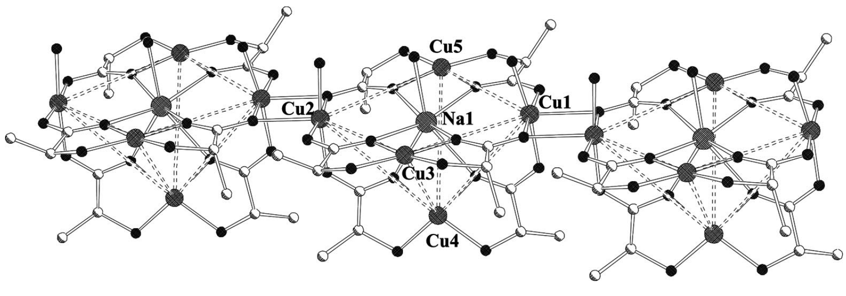


Figure 4. Structure of the cationic chain of **3**.

crease in temperature, the $\chi_m T$ values of three compounds increase slowly and a subsequent much sharper increase below ca. 30 K. The abrupt increase at low temperature is indicative of weak ferromagnetic coupling between the paramagnetic centers of the [Cu$_n$] unit, as confirmed by the positive Weiss constant (21.7, 18.8, 14.4 K for **1**, **2**, **3**, respectively).

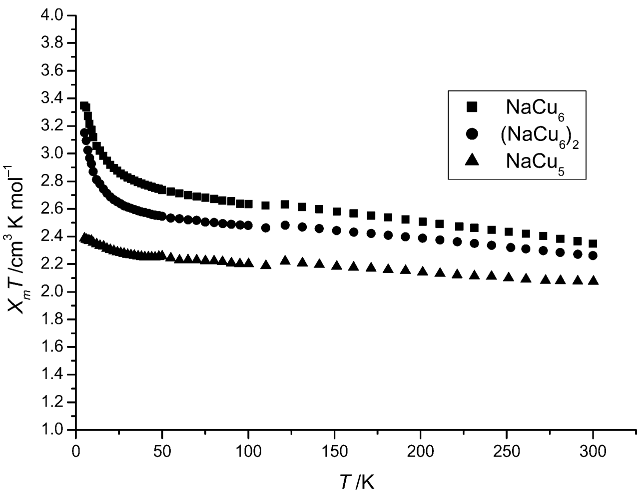


Figure 5. Temperature dependence of $\chi_m T$ for the three compounds.

From the magnetic behavior of compound **1** it must be considered that the only significant spin–spin interaction is the coupling between the axial Cu^{II} centers (Cu1 and Cu2) and the equatorial Cu^{II} ions of the hexanuclear unit. As was shown in the few well-characterized Cu^{II} complexes through the *syn–anti* carboxylato bridge, such as [Na⊂{Cu$_6$(Thr)$_8$(H$_2$O)$_2$(ClO$_4$)$_4$}]·ClO$_4$·5H$_2$O[18b] and [Na⊂Cu$_6$(Pro)$_8$(ClO$_4$)$_5$CH$_3$OH]·H$_2$O,[19] weak ferromagnetic coupling was observed. By following the Heisenberg Spin-Hamiltonian model,[18b,19] the coupling constant between the equatorial Cu centers and the axial ones is ca. 0.64 cm^{-1}.

Two kinds of magnetic interactions must be considered to interpret the magnetic properties of **2** and **3**: the intracluster interactions inside each [Cu$_n$] unit and the intercluster interaction between adjacent [Cu$_n$] units. The intracluster interactions are similar to those in **1**. We can find that the sequence of the $\chi_m T$ value for the corresponding unit of the three compounds is: **1** > **2** > **3**, which suggests that the interaction between the cluster units within compounds **2** and **3** may be antiferromagnetic. This phenomenon is in agreement with their structural characteristics. The Cu–O–Cu angels within the Cu$_2$O$_2$ ring for the two compounds are all larger than 97.5°, which suggests that the interactions between the clusters of **2** and **3** are antiferromagnetic in nature with respective magnitudes of about 317 and 381 cm^{-1} according to the linear function proposed by Hatfield.[22]

Conclusions

In this paper, three compounds were obtained from controlling the proportion of Cu^{II} ions to L-alanine. The proportion of Cu to Ala plays an important role in the formation of the products. With an increasing Cu content, the Ala ligands will bind more Cu ions with the coordination mode varying from [3.1$_1$2$_{23}$1$_3$] to [4.2$_{12}$2$_{34}$1$_4$], which results in the conversion of the product from the NaCu$_6$ cluster to the dimer and further to the NaCu$_5$ chain. These compounds can be viewed as a new type of spherical macrotricyclic metallacryptate. Although the metal cage of **3** is incomplete, it also has strong encapsulating ability for sodium ion. The magnetic susceptibility measurements indicate that all three clusters are ferromagnetic overall, although the intercluster interactions may be antiferromagnetic.

Experimental Section

General: All starting materials were of reagent grade and used without further purification. Elemental analyses were carried out by the Elemental Analysis Lab of our Institute. Magnetic measurements were carried out with a Quantum Design PPMS model 6000 magnetometer.

[Na⊂{Cu$_6$(Ala)$_8$(H$_2$O)(ClO$_4$)}]·4ClO$_4$·4H$_2$O (1): To an aqueous solution (15 mL) of Cu(ClO$_4$)$_2$·5H$_2$O (2.115 g, 6 mmol) was added L-alanine (0.624 g, 7 mmol). The pH value of the reaction mixture was carefully adjusted to about 6.0 by slow addition of NaOH (0.1 M) solution. After filtration, the solution was placed in a desiccator filled with phosphorus pentaoxide. Blue crystals (0.60 g) were obtained about a month later and isolated by filtration in 40.8% yield based on L-alanine. C$_{24}$H$_{56}$Cl$_5$Cu$_6$N$_8$NaO$_{40}$ (1678.25): calcd. C 17.18, H 3.36, N 6.68, Na 1.37; found C 16.77, H 3.74, N 6.44, Na 1.56.

Na[Na⊂{Cu$_6$(Ala)$_8$(ClO$_4$)}]$_2$·9ClO$_4$·8H$_2$O (2): The above procedure was repeated except that the proportion of the reactants was controlled: Cu(ClO$_4$)$_2$·5H$_2$O/L-alanine, 8:8. Yield: 0.63 g (36.2% based on L-alanine). C$_{48}$H$_{112}$Cl$_{11}$Cu$_{12}$N$_{16}$Na$_3$O$_{84}$ (3478.94): calcd. C 16.57, H 3.24, N 6.44, Na 1.98; found C 16.20, H 3.65, N 6.23, Na 2.17.

[Na⊂{Cu$_5$(Ala)$_6$(H$_2$O)$_3$}]$_n$·5n(ClO$_4$)·3n(H$_2$O) (3): The above procedure was repeated except that the proportion of the reactants was controlled: Cu(ClO$_4$)$_2$·5H$_2$O/L-alanine, 10:9. Yield: 0.94 g (42.5% based on L-alanine). C$_{18}$H$_{48}$Cl$_5$Cu$_5$N$_6$NaO$_{38}$ (1474.56): calcd. C 14.66, H 3.28, N 5.70; found C 14.50, H 2.61, N 5.46.

Crystallographic Studies: Intensity data for the three complexes were collected at 293(2) K with a Siemens Smart CCD diffractometer with Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods by using SHELXS-97[23] and refined by full-matrix least-squares methods by using SHELXL-97.[24] Anisotropic displacement parameters were refined for all non-hydrogen atoms except two oxygen atoms (O134, O182 in compound **2**). No attempt was made to locate the hydrogen atoms of water; the other hydrogen atoms were added in the riding model and not refined. Final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, and $Rw = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$, with $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. The crystallographic data are summarized in Table 1. CCDC-207784, -207785, and -207786 contain the supplementary

Table 1. Crystal data collection and structure refinement parameters for **1**–**3**.

	1[a]	**2**[b]	**3**[c]
Formula	$C_{24}H_{56}N_8O_{40}Cl_5Cu_6Na$	$C_{48}H_{112}N_{16}O_{84}Cl_{11}Cu_{12}Na_3$	$C_{18}H_{48}N_6O_{38}Cl_5Cu_5Na$
Formula weight	1678.25	3478.94	1474.56
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	*C*2	P1	P1
a / Å	18.5696(7)	12.8784(3)	9.8382(4)
b / Å	18.2633(7)	12.9517(4)	11.9417(4)
c / Å	18.1832(7)	19.7980(5)	12.3552(5)
α / °	90	105.448(1)	116.511(1)
β / °	90.047(1)	100.936(1)	99.776(1)
γ / °	90	91.780(1)	93.546(1)
V / Å^3	6166.7(4)	3113.51(14)	1264.37(8)
Z	4	1	1
$D_{calcd.}$ / g cm^{-3}	1.808	1.855	1.937
T / K	293(2)	293(2)	293(2)
$\lambda_{Mo\text{-}K\alpha}$ / Å	0.71073	0.71073	0.71073
μ / mm^{-1}	2.358	2.365	2.451
R_{int}	0.0291	0.0272	0.0228
$F(000)$	3384	1752	743
R[c]	0.0786	0.0852	0.0469
Rw[d]	0.1904	0.2215	0.1222
GOF	1.124	1.131	1.082
Max, min. $\Delta\rho$ / e Å^{-3}	0.001, 0.000	0.056, 0.005	0.000, 0.000

[a] For complex **1**: $a = 0.0862$; $b = 72.1049$. [b] For complex **2**: $a = 0.1134$; $b = 28.3509$. [c] For complex **3**: $a = 0.0799$; $b = 2.2501$. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $Rw = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma wF_o^4\}^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.

crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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