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New cyano-bridged complexes based on tetrahedral rhenium chalcocyanide clusters, Cu^{2+} cations, and polydentate amines

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Three new cyano-bridged compounds, *viz.*, $[\{Cu(en)\}\{Cu(NH_3)(en)\}Re_4Se_4(CN)_{12}]\cdot5H_2O$ (**1**), $[\{Cu(dien)\}_2Re_4Te_4(CN)_{12}]\cdot9H_2O$ (**2**), and $[\{Cu(trien)\}_2Re_4Se_4(CN)_{12}]\cdot5H_2O$ (**3**), were synthesized by the reactions of the tetrahedral rhenium chalcocyanide cluster complexes $K_4[Re_4Q_4(CN)_{12}]$ (Q = Se or Te) with copper(II) cations in aqueous solutions containing ethylenediamine (en), diethylenetriamine (dien), or triethylenetetraamine (trien), respectively. Complex **1** has a ladder-tubular-like polymeric structure, in which two infinite chains are linked to each other by Re—CN—Cu bridges, compound **2** has a polymeric chain structure, and compound **3** has a molecular structure. The structures of all complexes were established by X-ray diffraction analysis.

Key words: rhenium, tetrahedral chalcocyanide clusters, copper, cyanide bridges, coordination polymers, polydentate polyamines, crystal structure, X-ray diffraction analysis.

In recent years, the reactions of rhenium chalcocyanide cluster complexes with 3d-transition metal cations have attracted considerable attention.[1—4] Due to the ambident character, the CN group can serve as a bridging ligand to give polynuclear compounds of different dimensionality, *viz.*, framework,[2,5—8] layered,[1,9—11] chain,[12—15] or molecular compounds.[14,16] The use of polydentate ligands offers additional possibilities for controlling the dimensionality of the cyano-bridged compounds.[17—21] In recent years, we have carried out systematic studies of the synthesis of cyano-bridged coordination polymers based on the tetrahedral rhenium cluster complexes $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = S, Se, or Te) and 3d-metal complexes with N-donor ligands. The reactions of copper ammonium complexes with $K_4[Re_4Q_4(CN)_{12}]$ (Q = S, Se, or Te) were demonstrated to give chain structures,[15] whereas the reaction of the copper chelate complex $Cu(en)_2Cl_2$ (en is ethylenediamine) with $K_4[Re_4Te_4(CN)_{12}]$ in an ammonium medium afforded a molecular compound.[21] Investigation of the Cu^{2+}—dien—$[Re_4Q_4(CN)_{12}]^{4-}$ system (dien is diethylenetriamine) showed that both molecular and polymeric structures are produced depending on the composition of the solution.[20] In continuation of these studies, we examined the formation of such complexes in relation to the dentation of the N-donor ligand coordinated to the Cu atom at a constant Cu : ligand ratio of 1 : 1. We used en, dien, and triethylenetetraamine (trien) as the chelating ligands.

Results and Discussion

Complex **1** was prepared by the reaction of an aqueous solution of $K_4[Re_4Se_4(CN)_{12}]$ with an ammonium solu-

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tion of $CuCl_2$ containing en. The reaction with the use of an aqueous solution of $K_4[Re_4Te_4(CN)_{12}]$, an ammonium solution of $CuCl_2$, and dien as the starting reagents produced polymeric complex **2**. Analogously, molecular complex **3** was synthesized starting from $K_4[Re_4Se_4(CN)_{12}]$, trien, and $CuCl_2$. The structures of these three compounds were established by X-ray diffraction analysis.

Compound **1** has a polymeric structure, in which two infinite chains extended along the crystallographic axis *b* are linked to each other by the Re(1)—CN—Cu(1) bridges to form a ladder-like tubular motif (Fig. 1, *a*). The cluster anion $[Re_4Se_4(CN)_{12}]^{4-}$ in complex **1** is structurally similar to that in the starting salt.[5] The cluster core $\{Re_4Se_4\}$ is formed by four Re atoms occupying the vertices of the tetrahedron and four μ_3-bridging Se atoms; the Re—Re and Re—(μ_3-Se) distances vary in ranges of 2.797(1)—2.812(1) and 2.452(1)—2.467(1) Å, respectively. Each Re atom is coordinated by three terminal CN ligands. The cationic moiety of this compound is formed by two crystallographically independent Cu atoms, which lie on mirror planes and have different coordination environments. The Cu(1) atom is coordinated by two amino groups of the ethylenediamine molecule in a chelate fashion and by three N atoms of the cyanide groups of three different cluster anions. Therefore, the Cu(1) atom serves as a bridge linking three anions. The coordination environment about this atom is a distorted square pyramid, in which the apical N atom (N(2)) of the CN ligand is at a distance of 2.28(2) Å from the Cu(1) atom, and the lengths of the equatorial bonds with two other nitrogen atoms of CN groups and two N atoms of the en molecule are 1.97(1) Å and 2.02(1) Å, respectively (Fig. 1, *b*). The Cu(2) atom is also in a tetragonal-pyramidal environment but, unlike the Cu(1) atom, it serves as a bridge for two cluster anions. The Cu(2) atom is coordinated by two equivalent nitrogen atoms of CN groups (Cu(2)—N(6), 2.13(1) Å), two amino groups of the en molecule, and the NH_3 molecule (Cu—N, 1.95(2)—2.05(2) Å). The en molecule is disordered over two positions related by a sym-

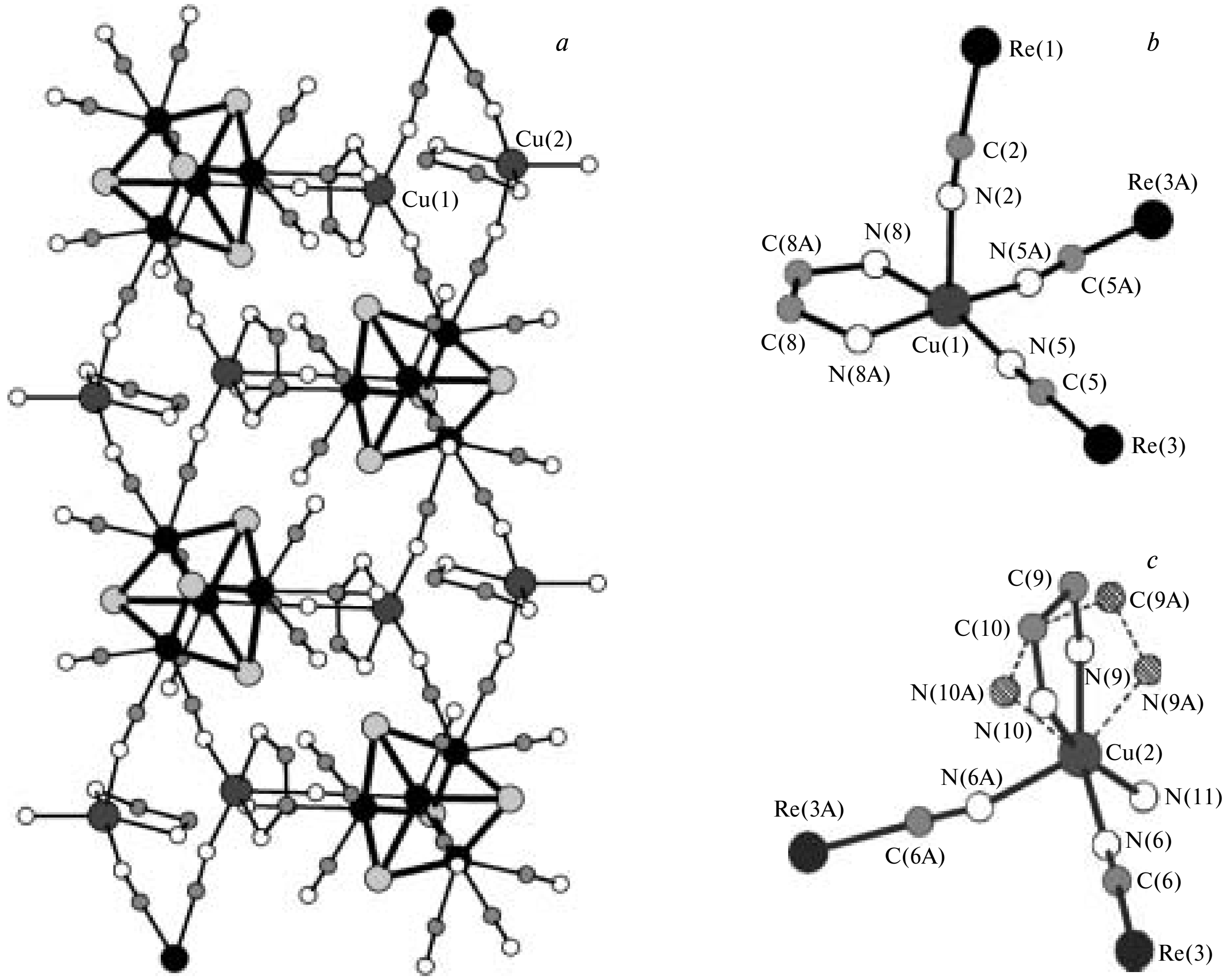

Fig. 1. Fragment of the structure of complex **1** (*a*) and the coordination environments of the Cu(1) (*b*) and Cu(2) (*c*) atoms in the structure of **1**.

metry plane. The probable conformation of the ring is Cu(2)—N(9)(+)—C(9)(+)—C(10)—N(10)(–)—Cu(2) (Fig. 1, *c*), where the plus and minus signs denote the positions above and below the symmetry plane relative to which the en molecule is disordered (for the second orientation, the plus and minus signs are interchanged). Therefore, the coordination polyhedron of the Cu(2) atom has two equivalent orientations. The C(10) and N(11) atoms are common to both orientations, and the bridging cyanide anions alternately serve as the axial ligands.

The crystal structure of complex **1** differs substantially from that of the $[\{Cu(en)_2\}_2Re_4Te_4(CN)_{12}] \cdot 5H_2O$ compound (**4**), which has been isolated earlier[17] from an analogous system. In compound **1**, the Cu atom is coordinated by only one ethylenediamine molecule, whereas the Cu atom in compound **4** is coordinated by two ethylenediamine molecules, resulting in a radical change in the structure. Compound **1** has a rather complex polymeric structure, whereas the isolated molecules of the $[\{Cu(en)_2\}_2Re_4Te_4(CN)_{12}]$ complex in the crystal of **4** are linked only through hydrogen bonds involving the H_2O molecules.

The cluster anion $[Re_4Te_4(CN)_{12}]^{4-}$ in compound **2** is structurally similar to the anion in the starting salt.[22] The Re—Re and Re—(μ_3-Te) distances in the cluster core $\{Re_4Te_4\}$ are in ranges of 2.855(1)—2.8786(9) and 2.6288(7)—2.646(1) Å, respectively. The cluster anions are linked to each other through two complex cations $\{Cu(dien)\}^{2+}$. An alternation of the ...2 Cu(dien)—cluster—2 Cu(dien)... fragments gives rise to a coordination-chain polymer, whose structure is shown in Fig. 2, *a*. The coordination polyhedron of the Cu atoms with a coordination number of 5 is a distorted square pyramid (Fig. 2, *b*) formed by three N atoms of the tridentate dien ligand and two nitrogen atoms of the CN ligands. One of the cyanide groups occupies the apical position in the coordination polyhedron of the Cu atom (Cu(1)—N(41), 2.232(6) Å), whereas another cyanide group is in the equatorial position (Cu(1)—N(31), 1.977(6) Å). The bond lengths between the Cu atoms and the N atoms of the dien molecule are in a range of 1.985(8)—2.019(7) Å.

Earlier, we have described analogous chain structures for the $[\{Cu(NH_3)_3\}_2Re_4Q_4(CN)_{12}] \cdot xH_2O$ compounds (Q = S or Se), in which the cluster anions are linked to each other by two cationic fragments $\{Cu(NH_3)_3\}^{2+}$.[15] In the ammonium analog, four CN groups of one cluster anion involved in the formation of the polymeric structure are coordinated to two Re atoms (2 + 2), whereas the bridging CN ligands in the compound with dien are coordinated to three Re atoms (2 + 1 + 1).

In the structure of compound **3**, two crystallographically independent $[Cu(trien)]^{2+}$ cations are bound to the nitrogen atoms of the CN ligands of one $[Re_4Se_4(CN)_{12}]^{4-}$ anion, in which the Re—Re and Re—(μ_3-Se) distances vary in ranges of 2.7923(9)—2.8083(9) and

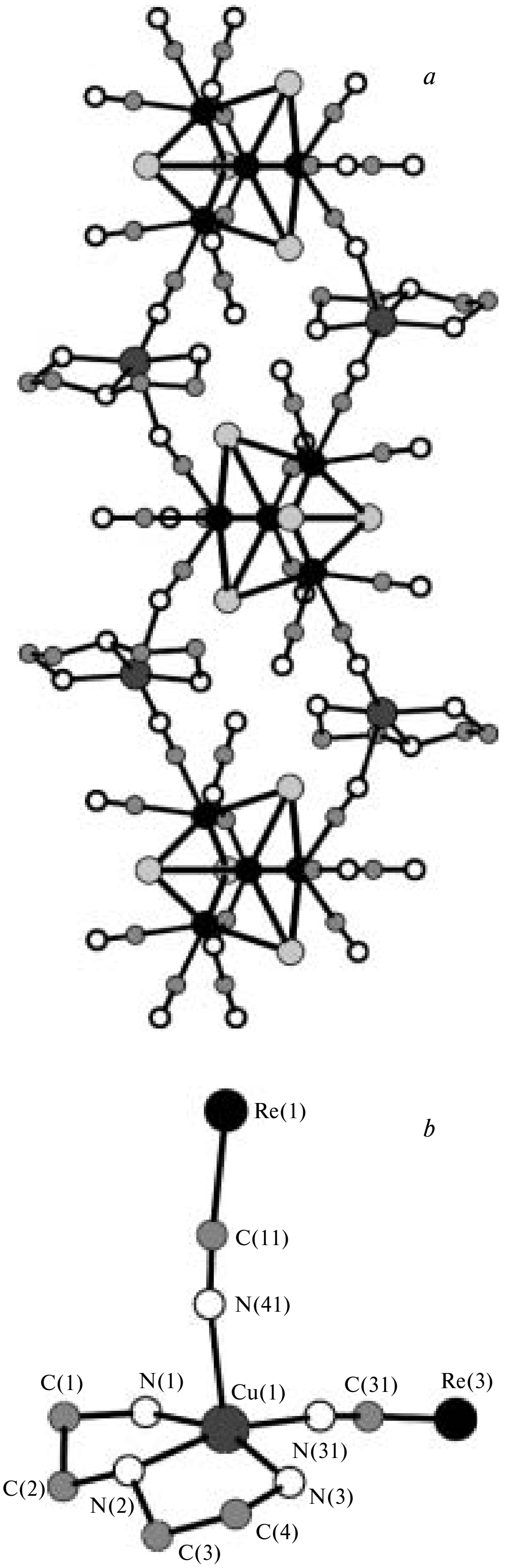

Fig. 2. Fragment of the structure of complex **2** (*a*) and the coordination environment of the Cu atoms in the structure of **2** (*b*).

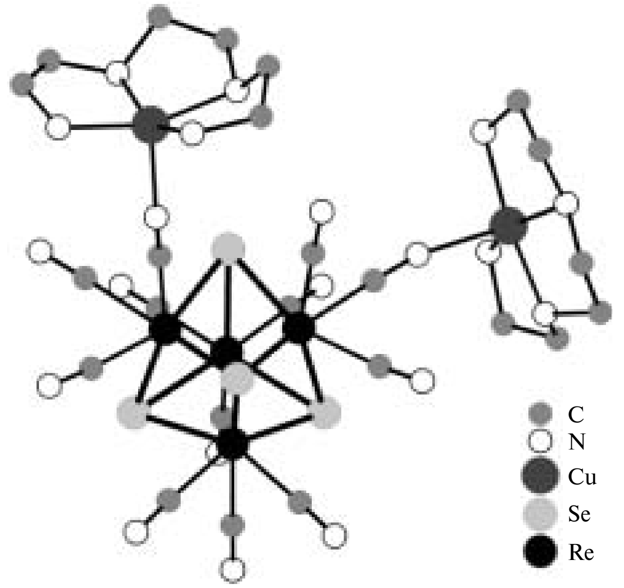

Fig. 3. Structure of molecular complex **3**.

2.453(1)—2.478(2) Å, respectively. The coordination polyhedron of each Cu atom (coordination number is 5) is a square pyramid with four N atoms of the tetradentate trien ligand located in the base (bond lengths are in a range of 1.98(1)—2.03(1) Å) and one N atom of the bridging cyanide group of the cluster anion in the axial position (Cu—N, 2.21(1) and 2.15(1) Å). As a result, the molecular complex $[\{Cu(trien)\}_2Re_4Se_4(CN)_{12}]$ is formed (Fig. 3). Compound **3** has a structure analogous to that of the molecular complex $[\{Cu(dien)(NH_3)\}_2Re_4Se_4(CN)_{12}] \cdot 2.5H_2O$,[20] in which the dien and NH_3 molecules are located in the equatorial planes of the polyhedra of the copper cations.

A comparison of the structures of the three compounds under study shows that there is a particular relationship between the dentation of the chelating ligand and the degree of polymerization of the crystal structure. In all three structures, the copper atoms are in a square-pyramidal environment, in which the polydentate ligands occupy two, three, and four coordination sites in compounds **1**, **2**, and **3**, respectively. In this series, the coordination topological motif of the structure gradually becomes simpler, resulting finally in the molecular structure. Presumably, this fact can be used for the directed synthesis and control over the dimensionality of new polynuclear cyano-bridged coordination compounds based on cluster cyano complexes of transition metals and 3d-metal complexes with N-donor ligands.

Experimental

The $K_4[Re_4Te_4(CN)_{12}] \cdot 5H_2O$ complex was synthesized by the reaction of $Re_4Te_4(TeCl_2)_4Cl_8$ with KCN in an aqueous solution.[22] The selenium analog was prepared by the reaction of $Re_4Se_4(TeCl_2)_4Cl_8$ with KCN.[5] The $Re_4Q_4(TeCl_2)_4Cl_8$ cluster (Q = Te) was synthesized by the reaction of $ReCl_5$ with elemental Te. The selenium analog was prepared by the reaction with a mixture of elemental Te and Se.[23] Other reagents were commercial compounds.

The IR spectra were recorded on a Bruker IFS-85 Fourier-transform IR spectrometer. Elemental analysis was carried out on Carlo Erba 1106 (complexes **1** and **2**) and Vario EL (complex **3**) instruments.

Dodecacyanotetra-μ₃-selenidotetrarhenium(Re—Re){aminoethylenediaminecopper(II)}{ethylenediaminecopper(II)} pentahydrate, $[\{Cu(en)\}\{Cu(NH_3)(en)\}Re_4Se_4(CN)_{12}] \cdot 5H_2O$ (1). An aqueous ammonium solution (5 mL) containing $CuCl_2$ (0.091 mmol) and en was added to a solution of $K_4[Re_4Se_4(CN)_{12}] \cdot 5H_2O$ (0.019 mmol) in water (5 mL). The resulting solution was concentrated at ~20 °C for two weeks. The dark crystals that formed were filtered off and dried in air. The yield was 0.021 g (65%). Found (%): C, 11.7; H, 1.85; N, 13.9. $C_{16}H_{29}Cu_2N_{17}O_4Re_4Se_4$. Calculated (%): C, 11.2; H, 1.59; N, 13.9. IR, ν/cm^{-1}: 2183 m, 2145 s (CN).

Dodecacyanotetra-μ₃-telluridotetrarhenium(Re—Re)bis{diethylenetriaminecopper(II)} nonahydrate, $[\{Cu(dien)\}_2Re_4Te_4(CN)_{12}] \cdot 9H_2O$ (2). An aqueous ammonium solution (5 mL) containing $CuCl_2$ (0.076 mmol) and dien was added to a solution of $K_4[Re_4Te_4(CN)_{12}] \cdot 5H_2O$ (0.017 mmol) in water (5 mL). The resulting solution was concentrated at ~20 °C for four weeks. The dark crystals that formed were filtered off and dried in air. The yield was 0.031 g (91%). Found (%): C, 11.9; H, 1.87; N, 12.6. $C_{20}H_{44}Cu_2N_{18}O_9Re_4Te_4$. Calculated (%): C, 11.6; H, 2.15; N, 12.2. IR, ν/cm^{-1}: 2184 m, 2162 m, 2138 s (CN).

Dodecacyanotetra-μ₃-selenidotetrarhenium(Re—Re)bis{triethylenetetraaminecopper(II)} pentahydrate, $[\{Cu(trien)\}_2Re_4Se_4(CN)_{12}] \cdot 5H_2O$ (3). An aqueous ammonium solution (5 mL) containing $CuCl_2$ (0.065 mmol) and trien was added to a solution of $K_4[Re_4Se_4(CN)_{12}] \cdot 5H_2O$ (0.019 mmol) in water (5 mL). The resulting solution was concentrated at ~20 °C for four weeks. The dark crystals that formed were filtered off and dried in air. The yield was 0.033 g (84%). Found (%): C, 15.3; H, 2.45; N, 14.7. $C_{24}H_{46}Cu_2N_{20}O_5Re_4Se_4$. Calculated (%): C, 15.3; H, 2.46; N, 14.9. IR, ν/cm^{-1}: 2184 w, 2146 s (CN).

X-ray diffraction study. The X-ray diffraction data for compounds **1**, **2**, and **3** were collected according to a standard procedure at ~20 °C on single-crystal automated Enraf-Nonius CAD-4 (compound **1**), Nonius Kappa CCD (compound **2**), and Siemens P4 (compound **3**) diffractometers (Mo-Kα radiation, λ = 0.71073 Å, graphite monochromator). The measured intensities of reflections for complexes **1** and **3** were corrected for absorption using azimuth scanning curves. For complex **2**, the absorption correction was applied taking into account the crystal shape with the use of the GAUSSIAN program.[24] The structures were solved by direct methods followed by calculations of difference Fourier syntheses and refinement of the positional and anisotropic displacement parameters of the atoms by the full-matrix least-squares method using the SHELXL-97 program package.[25,26] The positions of the H atoms in the water molecules were not revealed. The positions of the hydrogen atoms in molecules **2** and **3** were calculated geometrically. Selected characteristics of X-ray diffraction study and structure refinement are given in Table 1.

Table 1. Crystallographic data for complexes **1**, **2**, and **3**

Parameter	**1**	**2**	**3**
Empirical formula	$C_{16}H_{29}Cu_2N_{17}O_5Re_4Se_4$	$C_{20}H_{44}Cu_2N_{18}O_9Re_4Te_4$	$C_{24}H_{46}Cu_2N_{20}O_5Re_4Se_4$
Molecular weight	1727.28	2063.01	1882.53
Crystal dimensions/mm	0.08×0.16×0.34	0.28×0.06×0.04	0.10×0.15×0.60
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	*C2/m*	*Pcmn*	$P2_1n$
a/Å	26.910(3)	9.643(5)	14.582(3)
b/Å	10.925(1)	18.575(5)	15.694(3)
c/Å	12.855(4)	26.572(5)	21.400(4)
β/deg	102.74(1)	—	99.01(3)
V/Å^3	3686(1)	4760(3)	4837.0(17)
Z	4	8	4
d_{calc}/mg m^{-3}	3.112	2.879	2.585
μ/mm^{-1}	18.22	13.472	13.898
Ranges of *h, k, l* indices	$-34 \le h \le 34$,	$-15 \le h \le 15$,	$0 \le h \le 17$,
	$0 \le k \le 14$,	$-29 \le k \le 29$,	$0 \le k \le 18$,
	$-16 \le l \le 0$	$-42 \le l \le 42$	$-25 \le l \le 25$
Transmission coefficients	0.0629, 0.3235	0.0654, 0.4428	0.21377, 0.13882
Number of measured/ independent reflections	4118/3947	82254/10699	8833/8475
R_{int}	0.0287	0.1185	0.0390
Number of parameters in refinement	251	291	532
R ($I > 2\sigma$)			
R_1	0.0329	0.0495	0.0502
wR_2	0.0808	0.1123	0.0926
R (all reflections)			
R_1	0.0544	0.0969	0.0955
wR_2	0.0860	0.1333	0.1074

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