Synthesis and Structures of Compounds Based on Chalcocyanide Tetranuclear Rhenium Clusters: Bonding Cluster Complexes by diene-Bridged Cu^{II} Units

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Six new tetrahedral chalcocyanide cluster compounds, $[\{Cu_2(dien)_3\}Re_4S_4(CN)_{12}]$ (**1**), $[\{Cu(dien)(NH_3)\}_2Re_4Se_4(CN)_{12}]\cdot 2.5H_2O$ (**2**), $[\{Cu_2(dien)_3\}Re_4Q_4(CN)_{12}]\cdot nH_2O$ (Q = Se (**3**), Te (**4**)] and $[K(H_2O)_2]_2[\{Cu_3(dien)_4\}\{Re_4Q_4(CN)_{12}\}_2]\cdot 8H_2O$ where Q = Se (**5**), Te (**6**) (dien = diethylenetriamine), have been synthesized by treating aqueous solutions of the salt-like cluster compounds $K_4Re_4Q_4(CN)_{12}\cdot nH_2O$ with solutions of copper(II) chloride in aqueous ammonia containing diethylenetriamine. All six compounds have been characterized by single-crystal X-ray diffraction analysis. Compound **1** has a chain-like polymeric structure; orthorhombic, space group $Pmn2_1$. Compound **2** has a molecular structure; triclinic, space group $P\bar{1}$. Compounds **3** and **4** are isostructural and also exhibit molecular structures; monoclinic, space group $P2_1/n$. Compounds **5** and **6** are isostructural and display a cross-bridged chain-like polymeric structure; triclinic, space group $P\bar{1}$.

Introduction

Considerable recent research has been devoted to designing new polymeric compounds with extended structures based on rhenium cluster compounds.[1−4] Such compounds may have interesting catalytic, magnetic or zeolitic properties. The directional choice of cluster/ligand and cluster/cation combinations helps to control both the topology and the dimensionality of solids. A useful approach for this purpose consists of assembling two building blocks, which are often cluster complexes with terminal ligands that can act as bridges and transition metal complexes with vacant or readily substituted coordination sites. Typical examples are Re cluster chalcocyanide complexes with terminal CN ligands and aqua or amine transition metal complexes.[5−13] The next logical step in such investigations is to use polydentate ligands to block some of the available positions around the transition metal atom, so as to control the positions available for coordination with the CN ligands. The first examples of such complexes were published recently.[14] Here we present six complexes containing $[Re_4Q_4(CN)_{12}]^{4-}$ cluster anions and Cu^{II} cations, coordinated by dien ligands and bridging CN ligands of the cluster units. Our data demonstrate the significant dependence of the stoichiometry and structure of the product on the reaction conditions and internal ligands of the cluster unit. We have prepared one chain-like coordination polymer $[\{Cu_2(dien)_3\}_2Re_4S_4(CN)_{12}]$ (**1**) (dien = diethylenetriamine), three molecular complexes $[\{Cu(dien)(NH_3)\}_2Re_4Se_4(CN)_{12}]$ (**2**) and $[\{Cu_2(dien)_3\}Re_4Q_4(CN)_{12}]\cdot 8H_2O$ [Q = Se (**3**), Q = Te (**4**)], and two polymeric complexes $[K(H_2O)_2]_2[\{Cu_3(dien)_4\}\{Re_4Q_4(CN)_{12}\}_2]\cdot 8H_2O$ [Q = Se (**5**), Q = Te (**6**)]. One of the most interesting features of the polymeric complexes is their construction by dien-bridging of Cu^{II} atoms.

Results

Syntheses

The chain-like one-dimensional compound **1** was synthesized by treating an aqueous solution of the Re_4 thiocyanide cluster $K_4[Re_4S_4(CN)_{12}]$ with an ammonia solution of $CuCl_2$ and dien. Two molecular complexes, **2** and **3**, and the polymeric compound **5** were obtained in a similar manner using $K_4[Re_4Se_4(CN)_{12}]$ as a starting material. Analogously, the molecular complex **4** and the polymeric compound **6** were prepared using $K_4[Re_4Te_4(CN)_{12}]$ as a starting material. Thus, by performing the reactions with different ratios of the starting components, complexes with differing compositions and structures were obtained for cluster anions $[Re_4Q_4(CN)_{12}]^{4-}$ with the Q = Se and Te.

These investigations extend our earlier studies on the reactions of $K_4Re_4Te_4(CN)_{12}$ with aqua or ammine complexes of the transition metals, which yield cyano-bridged cluster complexes with differing dimensionalities. Transition

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metal atoms in such complexes are coordinated by the N atoms of the cyanide ligands and by the N or O atoms, respectively, of ammonia and water molecules. Recent work[14] has shown that some of the coordination sites around the transition metal atom may effectively be blocked by bidentate ligands such as ethylenediamine.

Structures

All six compounds have been characterized by single-crystal X-ray diffraction. Compound **1** is polymeric, with the cluster anions $[Re_4S_4(CN)_{12}]^{4-}$ bridged by the cationic chains $[(dien)Cu{-}dien{-}Cu(dien)]^{4+}$ (Figure 1). The structure of the $[Re_4S_4(CN)_{12}]^{4-}$ anion is similar to that in the starting material and related compounds. It contains an Re_4S_4 cubane-like cluster core formed from a nearly regular Re_4 tetrahedron, with Re−Re and Re−(μ_3-S) distances in the ranges 2.739(2)−2.767(1) and 2.337(7)−2.434(7) Å, respectively. Each Re atom is further ligated by three cyano ligands. Each Cu atom in the cationic chain-like building blocks is coordinated in a square-pyramidal manner (*CN* = 5) by three N atoms of the tridentate dien, with Cu−N distances of 1.94(2)−2.03(2) Å, one N atom of the bridging dien, with a Cu−N length of 1.97(2) Å, and by one N atom of a CN^- ligand of the cluster anion with a Cu−N length of 2.20(2) Å.

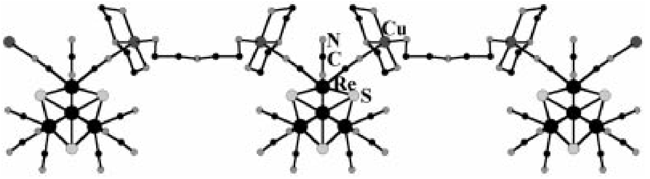

Figure 1. Chain fragment of the structure of compound **1**

In compound **2**, two $[Cu(dien)(NH_3)]^{2+}$ cations are coordinated to the N atoms of CN^- ligands of the $[Re_4Se_4(CN)_{12}]^{4-}$ anion (Figure 2). Each Cu atom is coordinated by the three N atoms of the dien ligand, with Cu−N distances of 2.01(1)−2.05(1) Å, one atom of an NH_3 ligand, with Cu−N distances of 1.99(1) and 2.03(1) Å, and by one N atom of a bridging CN^- ligand of the cluster anion with Cu−N distances of 2.38(1) and 2.19(1) Å. Once again the coordination number of each Cu is 5, and the copper atoms exhibit square-pyramidal coordination spheres with an axial cyanide nitrogen atom. Both $\{Cu(dien)(NH_3)\}^{2+}$ cations are coordinated to the same Re_4 cluster anion $[Re_4Se_4(CN)_{12}]^{4-}$. In the cluster anion the Re−Re and Re−(μ_3-S) distances are 2.792(1)−2.811(1) and 2.448(2)−2.470(2) Å, respectively, and are similar to that in the starting compound.

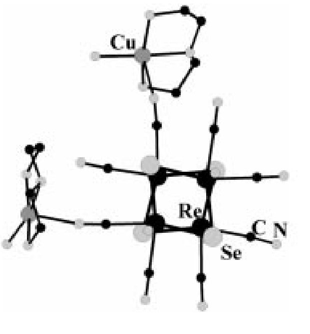

Figure 2. View of the $[\{Cu(dien)(NH_3)\}_2Re_4Se_4(CN)_{12}]$ molecule in compound **2**

Compounds $[\{Cu_2(dien)_3\}Re_4Q_4(CN)_{12}]{\cdot}nH_2O$ [Q = Se (**3**) and Te (**4**)] are isostructural. Their compositions are similar to that of **1**, but their structures are slightly different. Whereas compound **1** has a chain-like polymeric structure (Figure 1), **3** and **4** are molecular (Figure 3) and contain cluster anions $[Re_4Q_4(CN)_{12}]^{4-}$ (Q = Se, Te) and non-bridging cationic $[Cu_2(dien)_3]^{4+}$ units. In **1** both Cu atoms are crystallographically equivalent and coordinated to N atoms of CN^- ligands of different clusters. In **3** and **4** the Cu atoms exhibit different coordination environments. One Cu atom has a similar arrangement to the Cu atom in compound **1**; the second Cu atom is coordinated by three N atoms of one dien ligand and by two N atoms of another dien ligand, which bridges the two Cu atoms of the cationic unit through its third N atom. Thus, both Cu atoms in $[Cu_2(dien)_3]^{4+}$ cation are five-coordinate and, once again, have square-pyramidal coordination spheres.

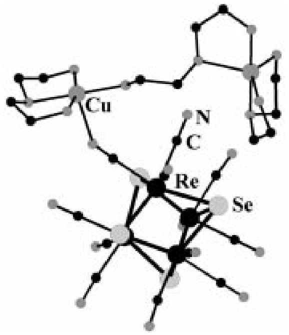

Figure 3. View of the $[\{Cu_2(dien)_3\}Re_4Se_4(CN)_{12}]$ molecule in compound **3**

$[K(H_2O)_2]_2[\{Cu_3(dien)_4\}\{Re_4Q_4(CN)_{12}\}_2]{\cdot}8H_2O$ [Q = Se (**5**) and Te (**6**)] are also isostructural. The structures of the anionic components $[Re_4Q_4(CN)_{12}]^{4-}$ are similar to those in the starting materials and related compounds. The Re−Re distances are 2.8624(9)−2.8821(11) Å (**5**) and 2.798(1)−2.809(1) Å (**6**), and the Re−(μ_3-Q) distances are 2.624(1)−2.649(1) Å (**5**) and 2.457(2)−2.484(2) Å (**6**). The secondary building unit of this structure is provided by the molecular complex $[\{Cu_3(dien)_4\}\{Re_4Te_4(CN)_{12}\}_2]$ (Figure 4), in which two cluster anions $[Re_4Te_4(CN)_{12}]^{4-}$ are bridged by the cation $[Cu_3(dien)_4]^{6+}$, which can be described as $[(dien)Cu{-}(dien)Cu(dien){-}Cu(dien)]$. There are two symmetry-equivalent Cu atoms, each coordinated by three N atoms of one dien ligand, one N atom of the bridging dien ligand, and by one N atom of a CN^- ligand of the $[Re_4Q_4(CN)_{12}]^{4-}$ anion [Cu−N distances are 2.009(9)−2.03(1), 2.011(9) and 2.376(9) Å for compound **5** and 2.03(1)−2.04(1), 2.04(1) and 2.38(1) Å for compound **6**]. The third Cu atom lies at the centre of this cation and is symmetrically coordinated by four N atoms of two bridging dien ligands with Cu−N distances of 1.999(9)−2.086(8) Å (**5**) and 2.02(1)−2.099(9) Å (**6**) and at the same time by two additional *trans*-situated N atoms of CN$^-$ ligands of two different anions (Figure 4). The opposite Cu−N distances are 2.579 Å for **5** and 2.581 Å for **6** and are slightly longer than the corresponding distances of five-coordinate Cu atoms. Thus, this Cu atom is octahedrally (*CN* = 6) coordinated and bridges the molecular units $[\{Cu_3(dien)_4\}\{Re_4Q_4(CN)_{12}\}_2]$ to construct the polymeric structure. The negative charge of this one-dimensional network is compensated by K$^+$ cations. N atoms of CN$^-$ ligands coordinate to these cations as shown in Figure 5.

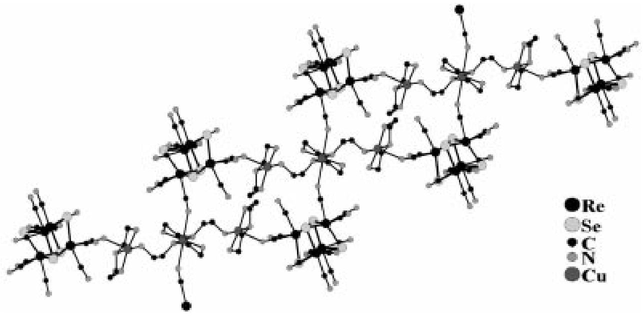

Figure 4. Anionic connectivity pattern in the crystal structure of compound **5**

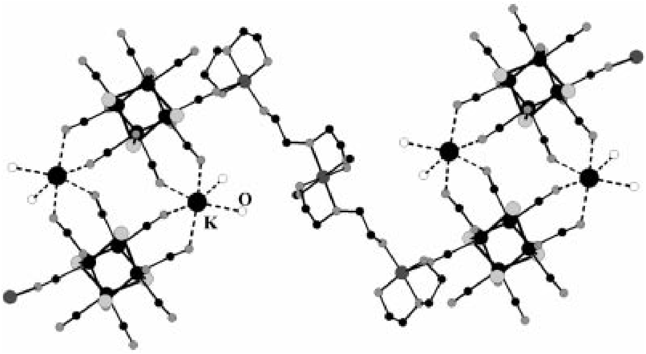

Figure 5. $[\{Cu_3(dien)_4\}\{Re_4Se_4(CN)_{12}\}_2]^{2-}$ secondary building unit in the crystal structure of compound **5** with associated potassium cations

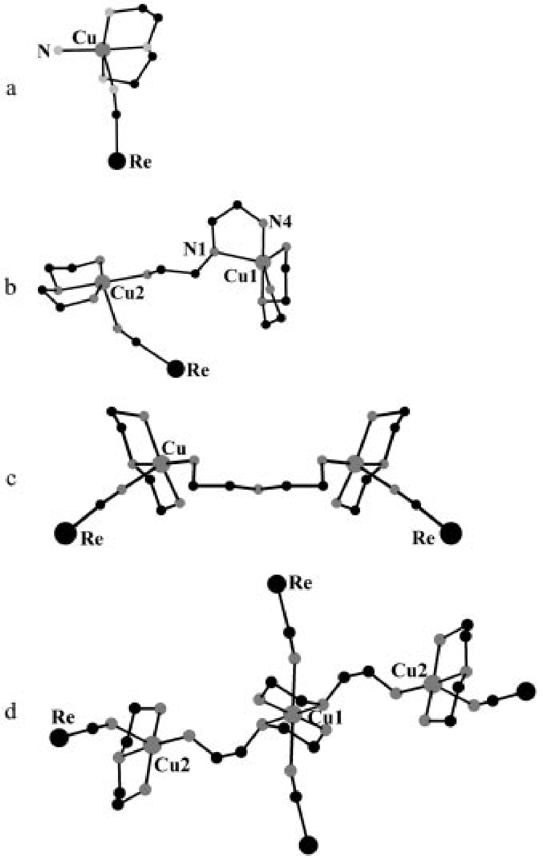

Figure 6. Ligand environment of Cu atoms: a (in **2**), b (in **3**, **4**), c (in **1**) and d (in **5**, **6**)

In compounds **1**, **5** and **6** Cu atoms bridged by dien ligands are bonded to cluster anions, whereas in **3** and **4** the complex cation $\{Cu_2(dien)_3\}$ is coordinated to one cluster anion only (Figure 6). Such coordinations have not previously been observed in Cu complexes; in all known similar complexes three N atoms of the dien ligand are always coordinated to one Cu atom as, for example, in $[Cu(dien)]_3[Fe(CN)_6]_2{\cdot}6H_2O$.[15] There are only two known examples of metal compounds (both Ag-containing complexes) with bridging dien ligands.[16]

From the structure analyses we conclude that the coordination of copper atoms is very important: it determines not only the stoichiometry but also the main features of the crystal structure. Evidently, in solutions of these systems, which contain two competitive N-donor ligands, NH$_3$ and dien, some cationic complexes − monomeric $[Cu(NH_3)(dien)]^{2+}$, and oligomeric $[(dien)Cu-(\mu\text{-}dien)-Cu(dien)]^{4+}$ and $[(dien)Cu-(\mu\text{-}dien)-Cu-(\mu\text{-}dien)-Cu(dien)]^{6+}$ are formed. The formation of oligomers can be explained by a deficiency of ligands in the coordination sphere of Cu^{2+} of simple complexes with stoichiometry [Cu(dien)] (dien has three N-donor atoms only). Copper atoms of similar complexes are unsaturated in their coordination and therefore tend to complete their environment by means of bond formation with other dien ligands. In the complexes **1**, **3**, **4** such interaction leads to oligomeric cations $[(dien)Cu-(\mu\text{-}dien)-Cu(dien)]^{4+}$ where an additional μ-dien ligand becomes a bridged one. If the concentration of Cu^{2+} ions is decreased (as in the syntheses of **5** and **6**), oligomeric cations with two bridged μ-dien ligands, $[(dien)Cu-(\mu\text{-}dien)-Cu-(\mu\text{-}dien)-Cu(dien)]^{6+}$, are formed. However, the copper atoms in such oligomers are again unsaturated − a reason for further interaction with CN ligands of the cluster anions.

As expected, the ratio of reagents is an important experimental factor that affects the composition of the resultant compounds. For example, for a Cu/dien ratio near 1:1, complex **2** is formed. If the concentration of dien is increased, complexes **1**, **3**−**6** with higher dien contents are realized. It is of interest that, although in all these reactions the concentration of Cu^{2+} ions was sufficient to form complexes containing only Cu^{2+} cations {the ratio Cu^{2+}/$[Re_4Q_4(CN)_{12}]^{4-} > 2$}, two compounds (**5** and **6**) were obtained that are crystallized with additional K^+ cations. This may be due to structural factors: these compounds contain longer oligomeric cations $[(dien)Cu-(\mu\text{-}dien)-Cu-(\mu\text{-}dien)-Cu(dien)]^{6+}$.

Comparison of complex **1** (Figure 6, c) with **3** and **4** (Figure 6, b) shows that the latter can be transformed into the structure of **1** by breaking the Cu1−N1(μ-dien) bond and then joining the CN group of the cluster complex to a vacated coordination site of the copper atom.

Experimental Section

Materials and Syntheses: All reagents were used as purchased. $[K_4Re_4Te_4(CN)_{12}]\cdot 5H_2O$ was synthesized by the reaction of $[Re_4Te_4(TeCl_2)_4Cl_8]$ with KCN in water.[17] Se and S analogues were synthesized by the reactions of $[Re_4Se_4(TeCl_2)_4Cl_8]$ and $[Re_4S_4(TeCl_2)_4Cl_8]$, respectively, with KCN as described for $[K_4Re_4Se_4(CN)_{12}]\cdot 6H_2O$.[12] $[Re_4Q_4(TeCl_2)_4Cl_8]$ (Q = Te, Se, S) were synthesized by the reaction of $ReCl_5$ with elemental Te or with a mixture of elemental Se or S with elemental Te.[18] FT-IR: Bruker IFS-85, Perkin−Elmer 1760X. Elemental analyses: Vario EL of Elementar Analysensysteme GmbH.

$[\{Cu_2(dien)_3\}Re_4S_4(CN)_{12}]$ (1): A solution of $CuCl_2$ (0.04 g) in concentrated aqueous ammonia (5 mL) was mixed with a solution of $[K_4Re_4S_4(CN)_{12}]\cdot 5H_2O$ (0.02 g) in water (5 mL). Diethylenetriamine (dien) (0.04 mL) was added to the reaction mixture and the resultant solution was kept for two weeks in a vessel covered by a watch glass. Dark red crystals that formed during this time were filtered off and dried on filter paper. Yield: 0.02 g (67%). $C_{24}H_{55}Cu_2N_{21}O_8Re_4S_4$ (2148.17): calcd. C 17.8, H 2.4, N 18.1, S 7.9; found C 17.5, H 2.9, N 17.9, S 7.6. IR (KBr): $\tilde{\nu}$ = 2180 (w), 2153 (s) [ν(CN)] cm^{-1}.

$[\{Cu(dien)(NH_3)\}_2Re_4Se_4(CN)_{12}]\cdot 2.5H_2O$ (2): A solution of $CuCl_2$ (0.030 g) in concentrated aqueous ammonia (2 mL) was mixed with a solution of $[K_4Re_4Se_4(CN)_{12}]\cdot 5H_2O$ (0.015 g) in water (2 mL); dien (0.02 mL) was added to the reaction mixture and the resultant solution was kept for two weeks in a vessel covered by a watch glass. Black crystals that formed during this time were filtered off and dried on filter paper. Yield: 0.014 g (82%). $C_{20}H_{37}Cu_2N_{20}O_{2.5}Re_4Se_4$ (1785.42): calcd. C 13.5, H 2.1, N 15.7; found C 13.4, H 2.0, N 15.7. IR (KBr): $\tilde{\nu}$ = 2145 cm^{-1}.

$[\{Cu_2(dien)_3\}Re_4Se_4(CN)_{12}]\cdot 8.25H_2O$ (3): A solution of $CuCl_2$ (0.020 g) in concentrated aqueous ammonia (2 mL) was mixed with a solution of $[K_4Re_4Se_4(CN)_{12}]\cdot 5H_2O$ (0.015 g) in water (2 mL); dien (0.04 mL) was added to the reaction mixture and the resultant solution was kept for one week in a vessel covered by a watch glass. Black needle-like crystals that formed during this time were filtered off and dried on filter paper. Yield: 0.012 g (67%). $C_{24}H_{55.5}Cu_2N_{21}O_{8.25}Re_4Se_4$ (1958.11): calcd. C 14.7, H 2.7, N 15.0; found C 15.0, H 2.5, N 15.2. IR (KBr): $\tilde{\nu}$ = 2142 [ν(CN)] cm^{-1}.

$[\{Cu_2(dien)_3\}Re_4Te_4(CN)_{12}]\cdot 8H_2O$ (4): A solution of $CuCl_2$ (0.015 g) in concentrated aqueous ammonia (2 mL) was mixed with a solution of $[K_4Re_4Te_4(CN)_{12}]\cdot 5H_2O$ (0.007 g) in water (2 mL); dien (0.04 mL) was added to the reaction mixture. The resultant solution was kept for two weeks in a vessel covered by a watch glass. Black needle-like crystals formed during this time were filtered off and dried on filter paper. Yield: 0.008 g (95%). $C_{24}H_{55}Cu_2N_{21}O_8Re_4Te_4$ (2148.17): calcd. C 13.4, H 2.6, N 13.7; found C 13.6, H 2.5, N 14.0. IR (KBr): $\tilde{\nu}$ = 2134 [ν(CN)] cm^{-1}.

$[K(H_2O)_2]_2[\{Cu_3(dien)_4\}\{Re_4Se_4(CN)_{12}\}_2]\cdot 8H_2O$ (5): A solution of $CuCl_2$ (0.005 g) and dien (0.04 mL) in concentrated aqueous ammonia (2 mL) was mixed with a solution of $[K_4Re_4Se_4(CN)_{12}]\cdot 5H_2O$ (0.015 g) in water (2 mL). The resultant solution was kept for two weeks in a vessel covered by a watch glass. Black crystals that formed during this time were filtered off and dried on filter paper. Yield: 0.013 g (76%). $C_{40}H_{76}Cu_3K_2N_{36}O_{12}Re_8Se_8$ (3643.47): calcd. C 13.2, H 2.1, N 13.8; found C 13.3, H 2.5, N 14.0. IR (KBr): $\tilde{\nu}$ = 2145 [ν(CN)] cm^{-1}.

$[K(H_2O)_2]_2[\{Cu_3(dien)_4\}\{Re_4Te_4(CN)_{12}\}_2]\cdot 8H_2O$ (6): A solution of $CuCl_2$ (0.005 g) in concentrated aqueous ammonia (2 mL) was mixed with a solution of $[K_4Re_4Te_4(CN)_{12}]\cdot 5H_2O$ (0.015 g) in water (2 mL); dien (0.04 mL) was added to the reaction mixture. The resultant solution was then kept for two weeks in a vessel covered by a watch glass. Black prismatic crystals that formed during this time were filtered off and dried on filter paper. Yield: 0.016 g (96%). $C_{40}H_{76}Cu_3K_2N_{36}O_{12}Re_8Te_8$ (4032.58): calcd. C 11.9, H 1.9, N 12.5; found C 12.0, H 1.9, N 13.6. IR (KBr): $\tilde{\nu}$ = 2136 [ν(CN)] cm^{-1}.

Crystallography: Single-crystal X-ray diffraction data were collected by standard techniques [Mo-K_α radiation (λ = 0.71073 Å), ω-scan mode] with Enraf-Nonius CAD4 (compound **1**) and Siemens P4 (compounds **2**−**6**) diffractometers under ambient conditions. Data were corrected for absorption with azimuthal scans. The structures were solved by direct methods and refined by least-squares methods against F^2. All non-hydrogen atoms were refined anisotropically taking into account all independent reflections. The positions of the hydrogen atoms of the dien groups were idealized; those of water molecules were not located. All calculations were carried out with an IBM PC using the SHELX-97 program package.[19,20]

1: Dark red prism, crystal dimensions 0.24 × 0.20 × 0.18 mm, orthorhombic, space group $Pmn2_1$, $Z = 2$, $a = 15.272(2)$, $b = 8.8743(9)$, $c = 17.946(3)$ Å, $V = 2432.2(6)$ Å^3, $\rho_{calcd.} = 2.215$ g cm^{-1}, $\mu = 10.986$ mm^{-1}, 4887 measured reflections, 4402 independent ($R_{int} = 0.0387$), $R(F) = 0.0392$ for 2673 reflection with $F_{hkl} \geq 4\sigma(F_{hkl})$ and $R_w(F^2) = 0.0963$ for all independent reflections. The absolute structure was established by use of the Flack parameter.

2: Black block, crystal dimension 0.22 × 0.22 × 0.65 mm, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 12.242(3)$, $b = 12.969(4)$, $c = 15.439(6)$ Å, $\alpha = 95.12(3)$, $\beta = 110.38(3)$, $\gamma = 114.02(2)$°, $V = 2020.8(11)$ Å^3, $\rho_{calcd.} = 2.934$ g cm^{-1}, $\mu = 16.620$ mm^{-1}, 7487 measured reflections, 7143 independent ($R_{int} = 0.0503$), $R(F) = 0.0465$ for 5824 reflections with $F_{hkl} \geq 4\sigma(F_{hkl})$ and $R_w(F^2) = 0.1243$ for all independent reflections.

3: Black needles, crystal dimensions 0.08 × 0.10 × 0.65 mm, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 13.839(3)$, $b = 15.181(3)$, $c = 24.015(4)$ Å, $\beta = 95.78(2)$°, $V = 5019.7(17)$ Å^3, $\rho_{calcd.} = 2.798$ g cm^{-1}, $\mu = 12.581$ mm^{-1}, 10444 measured reflections, 8941 independent ($R_{int} = 0.0589$), $R(F) = 0.0613$ for 5209 reflections with $F_{hkl} \geq 4\sigma(F_{hkl})$ and $R_w(F^2) = 0.1488$ for all independent reflections.

4: Black needle, crystal dimensions 0.14 × 0.14 × 0.4 mm, monoclinic, space group $P2_1/n$, $Z = 4$, $a = 13.844(3)$, $b = 15.288(6)$, $c = 24.194(6)$ Å, $\beta = 95.287(13)$°, $V = 5099(2)$ Å^3, $\rho_{calcd.} = 2.591$ g cm^{-1}, $\mu = 13.403$ mm^{-1}, 9221 measured reflections, 8828 independent ($R_{int} = 0.0463$), $R(F) = 0.0499$ for 5601 reflections with $F_{hkl} \geq 4\sigma(F_{hk})$ and $R_w(F^2) = 0.0952$ for all independent reflections.

5: Black plate, crystal dimensions 0.10 × 0.14 × 0.18 mm, triclinic, space group $P\bar{1}$, $Z = 1$, $a = 13.547(3)$, $b = 13.622(3)$, $c = 14.126(3)$ Å, $\alpha = 68.55(3)$, $\beta = 64.58(3)$, $\gamma = 87.69(3)°$, $Z = 1$, $V = 2170.2(7)$ Å^3, $\rho_{calcd.} = 2.788$ g cm^{-1}, $\mu = 15.340$ mm^{-1}, 7980 measured reflections, 7641 independent ($R_{int} = 0.0691$), $R(F) = 0.0552$ for 5413 reflections with $F_{hkl} \geq 4\sigma(F_{hkl})$ and $R_w(F^2) = 0.1311$ for all independent reflections.

6: Black plate, crystal dimensions 0.04 × 0.10 × 0.30 mm, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 13.619(3)$, $b = 13.660(3)$, $c = 14.166(3)$ Å, $\alpha = 68.33(2)$, $\beta = 64.94(1)$, $\gamma = 87.42(2)°$, $V = 2199.1(8)$ Å^3, $\rho_{calcd.} = 3.045$ g cm^{-1}, $\mu = 14.430$ mm^{-1}, 8090 measured reflections, 7748 independent ($R_{int} = 0.0244$), $R(F) = 0.0374$ for 6081 reflections with $F_{hkl} \geq 4\sigma(F_{hkl})$ and $R_w(F^2) = 0.0739$ for all independent reflections.

Acknowledgments

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