$[Re_6Q_7O(3,5\text{-}Me_2PzH)_6]Br_2\cdot 3,5\text{-}Me_2PzH$ (Q = S, Se) − New Octahedral Rhenium Cluster Complexes with Organic Ligands: Original Synthetic Approach and Unexpected Ligand Exchange in the Cluster Core

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Dedicated to Prof. Dr. Heinrich Oppermann on the occasion of his 70th birthday

Keywords: Rhenium / Cluster compounds / Ligand exchange / Organic ligands / Structure elucidation / Laser fluorescence spectroscopy

Two new octahedral rhenium cluster complexes, $[Re_6S_7O(3,5\text{-}Me_2PzH)_6]Br_2\cdot 3,5\text{-}Me_2PzH$ (**1**) and $[Re_6Se_7O(3,5\text{-}Me_2PzH)_6]Br_2\cdot 3,5\text{-}Me_2PzH$ (**2**), with the organic ligand 3,5-dimethylpyrazole (3,5-Me_2PzH), have been synthesised by reaction of rhenium chalcobromides $Cs_3[Re_6(\mu_3\text{-}Q_7Br)Br_6]$ (Q = S, Se) with molten dimethylpyrazole. During the reaction, all six apical bromine ligands of the cluster complexes are substituted by the organic ligand, which is coordinated through the aromatic nitrogen atom N2. Additionally, the inner ligand μ_3-Br in the cluster core $[Re_6(\mu_3\text{-}Q_7Br)]^{3+}$ is substituted by oxygen, giving cluster cores $[Re_6(\mu_3\text{-}Q_7O)]^{2+}$ with mixed chalcogen/oxygen ligands. Compounds **1** and **2** have been characterised by single-crystal X-ray diffraction analysis. They are isostructural and crystallise with four formula units in the unit cell. Absorption spectra and luminescence characteristics of these two cluster compounds have been investigated in methanol. Absorption starts below 400 nm. For both compounds, broad emissions were found. The fluorescence decays of the two compounds follow a diexponential decay behaviour. The main fluorescence intensity decays have longer fluorescence lifetimes of 3.07 ± 0.03 (**1**) and 3.96 ± 0.02 μs (**2**). Studying the thermal stability of both compounds in vacuo showed that the release of 3,5-dimethylpyrazole ligands begins near 200 °C, and decomposition, with the removal of 7 molecules of 3,5-Me_2PzH, is complete at 330 °C.

Introduction

The chemistry of the rhenium octahedral cluster compounds with the cluster core $\{Re_6Q_8\}^{2+}$ (Q = S, Se) coordinated by organic N- and P-donor ligands is in a stage of rapid development.[1−14] Such organic−inorganic hybrids show interesting electronic, optical and structural properties. Synthetic strategies span both simple cluster modification and more demanding programmed supramolecular arrays. The latter includes hydrogen-bonded and metal-assisted supramolecular networks based on rhenium clusters possessing nicotinamide, isonicotinamide, 3,5-pyridinedicarboxylic acid and 4,4′-dipyridine as apical organic ligands. Furthermore, the dendritic encapsulation of rhenium clusters by polyetheraryl dendrons having pyridine and pyridone units at the focal point has been realised. In all, there is an almost infinite variability regarding the structural modification of such rhenium clusters. This provides the opportunity to achieve properties useful for possible in vivo applications. Thus, it is very appealing to develop metallic drugs based on rhenium clusters. In this context, particularly porphyrin and modified dendritic rhenium clusters show promising luminescence properties for the development of photosensitizers that could be applied to photodynamic therapy.[15,16] Furthermore, rhenium clusters may play an important role as agents in photon activation therapy (PAT).[17] This relatively new treatment paradigm in cancer therapy requires a sufficiently high density of metals in target regions. This could be achieved by organic-inorganic rhenium cluster complexes.

Because of this background, we are especially interested in an efficient synthetic procedure to introduce organic ligands into the rhenium cluster core. Thus, a new synthetic

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DOI: 10.1002/ejic.200400465

approach for grafting N-donor ligands to octahedral rhenium cluster compounds has been developed. Here we report the preparation and crystal structures of two new rhenium octahedral cluster complexes, $[Re_6S_7O(3,5\text{-}Me_2PzH)_6]Br_2\cdot 3,5\text{-}Me_2PzH$ (**1**) and $[Re_6Se_7O(3,5\text{-}Me_2PzH)_6]Br_2\cdot 3,5\text{-}Me_2PzH$ (**2**), which were synthesised by the reaction of rhenium chalcobromides $Cs_3[Re_6(\mu_3\text{-}Q_7Br)Br_6]$ (Q = S, Se) with molten 3,5-dimethylpyrazole (3,5-Me_2PzH). The spectroscopic, photophysical and thermal properties of these cluster compounds are also discussed.

Results and Discussion

Syntheses

As a general rule, rhenium cluster compounds containing cluster cores $\{Re_6Q_8\}^{2+}$ (Q = S, Se) and apical organic ligands have been prepared by solution chemistry. A disadvantage of solution chemistry in such syntheses is the rather low rate of interaction and possible hydrolysis (in the case of aqueous solutions or non-anhydrous organic solvents), which limit synthetic resources for preparation of desirable compositions. To overcome these difficulties, we employed a new approach using molten ligands as reaction media for the synthesis of cluster complexes with organic ligands. We applied this method to the reaction of the rhenium cluster compounds $Cs_3[Re_6(\mu_3\text{-}Q_7Br)Br_6]$ (Q = S, Se) with 3,5-dimethylpyrazole as the organic ligand. In the anionic rhenium complexes $[Re_6(\mu_3\text{-}Q_7Br)Br_6]^{3-}$ (Q = S, Se) used, the octahedron Re_6 is surrounded by a cube of eight (μ_3-Q_7Br) atoms (so-called "inner" ligands). Such an "octahedron into cube" forms the cluster core $\{Re_6(\mu_3\text{-}Q_7Br)\}^{3+}$. The six apical positions in the cluster complexes $[Re_6(\mu_3\text{-}Q_7Br)Br_6]^{3-}$ are fully occupied by Br atoms, which are called "outer" ligands. The outer bromide ligands in similar complexes possess anticipated substitutional lability, whereas inner ligands are bonded more strongly. So we expected that in reactions of these clusters with dimethylpyrazole, the apical ligands could be substituted by organic ligands without any change in the cluster core $\{Re_6(\mu_3\text{-}Q_7Br)\}$ as the fundamental building block.

Experimental results show that indeed all apical Br atoms are substituted by organic ligands. On the other hand, an interesting feature of these reactions is an unexpected ligand exchange in the octahedral cluster core, namely the replacement of the inner μ_3-Br ligand by an oxygen atom. Such a substitution is rather unusual in the chemistry of octahedral clusters. The possible source of oxygen for such a substitution is the solvated molecules of H_2O in the starting complexes.

Few examples are known of the substitution of one or two μ_3-Cl ligands by oxygen in the cluster core of octahedral rhenium chalcohalide complexes, and examples of μ_3-Br substitution with oxygen were not found in the literature. The complexes containing two O atoms in the cluster cores $\{Re_6Se_4O_2Cl_2\}^{4+}$ [18] and $\{Re_6S_6O_2\}^{2+}$ [3] were obtained starting from $Re_6Se_4Cl_{10}$ and $[Re_6S_6Cl_8]^{2-}$, respectively. Complexes with the cluster core $\{Re_6S_5OCl_2\}^{2+}$ containing one O atom were obtained from the cluster anion $[Re_6S_5Cl_9]^-$.[19–21] There are two typical sources of oxygen in these reactions: $OSiMe_3$[3,19] or water. Water either came from wet solvent[18] or was added directly to the reaction mixture.[18,20] Here we succeeded in the preparation of oxochalcogenide complexes with a cluster core having the composition $\{Re_6Q_7O\}^{2+}$.

Structures

Compounds **1** and **2** have been characterised by single-crystal X-ray diffraction. The compounds are isostructural. The cluster cations $[Re_6Q_7O(3,5\text{-}Me_2PzH)_6]^{2+}$ (Q = S, Se) contain the Re_6 octahedron residing in a Q_7O pseudocube. There is no disorder in the present structures: seven corner positions of the Q_7O cube are occupied exclusively by S (**1**) or Se (**2**) atoms and one by an O atom. Due to the presence of the O atom in the cluster core $\{Re_6Q_8\}$, the Re_6 octahedrons in both compounds are slightly irregular. Re–Re distances between Re atoms coordinated by the μ_3-O atom are shorter than those for other Re atoms. Each Re atom is coordinated by a 3,5-Me_2PzH. The structure of a complete molecule is shown in Figure 1. The Re–Re distances range from 2.5210(7) to 2.5995(7) Å in **1** and from 2.5465(13) to 2.6386(14) Å in **2**; the Re–Q distances range from 2.392(3) to 2.417(3) Å in **1** and from 2.509(2) to 2.544(2) Å in **2**; the Re–O distances range from 2.114(8) to 2.129(8) Å in **1** and from 2.022(8) to 2.036(8) Å in **2**; the Re–N distances are 2.13(1)–2.16(1) (**1**) and 2.16(2)–2.21(2) Å (**2**). The Re–O distances in **1** are slightly longer than those found in $(Bu_4N)_2[Re_6S_5OCl_8]$ [2.08(1)–2.09(1) Å][19] or $(Bu_4N)_4[(Re_6S_5OCl_7)_2O]$ (average Re–O: 2.087(6) Å][20] and shorter than in $[Re_6S_6O_2(PPr_3)_6][Re_6S_6Cl_8]$, where Re–O distances are in

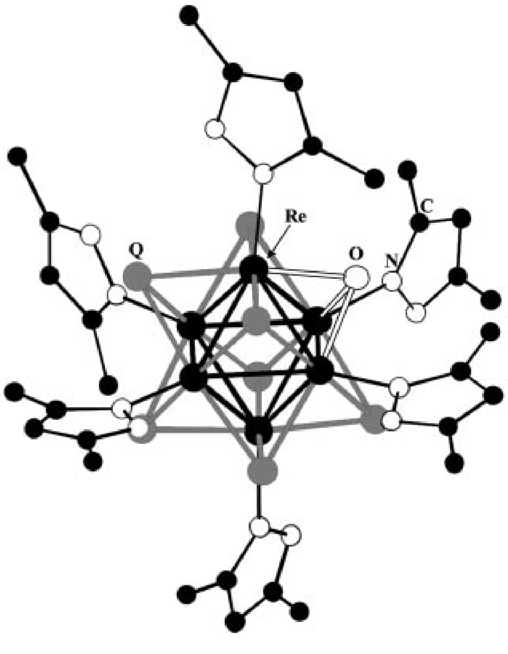

Figure 1. Structure of the cluster cation $[Re_6Q_7O(3,5\text{-}Me_2PzH)_6]^{2+}$ [Q = S (**1**), Se (**2**)]; all hydrogen atoms are omitted for clarity

the range 2.192(11)−2.226(11) Å.[3] The Re−O distances in **2** are the shortest among all known compounds of this type. Average Re−O distances in α- and β-$(Pr_4N)_2[Re_6Se_4O_2Cl_8]$ are equal to 2.083(14) and 2.094(19) Å, respectively.[18] There are two types of Br atoms in the structure: one bromine atom, Br1, is connected by hydrogen bonds to one cluster (Br···H−N distances are 3.25 and 3.31 Å in **1** and 3.24 and 3.28 Å in **2**) (Figure 2, a), whereas the other one, Br2, is bridged between two cluster cations with Br···H−N distances ranging from 3.41 to 3.68 Å in **1** and from 3.43 to 3.66 Å in **2** to form extended chains along the *a*-axes (Figure 2, b). Both compounds have additional noncoordinated molecules of 3,5-Me_2PzH.

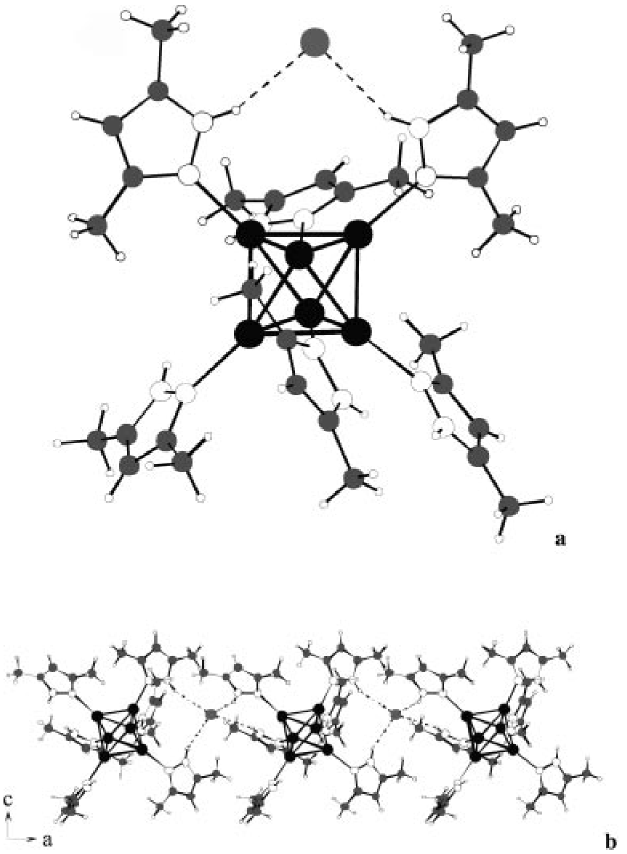

Figure 2. Connection of cluster cations with Br^- anions in compounds **1** and **2**: a) location of Br1; b) location of Br2 bridging cluster units; hydrogen bonds are denoted by dotted lines; all sulfur and oxygen atoms of the cluster core are omitted for clarity

Absorption Spectra and Luminescence Characteristics

Solutions (1.0×10^{-5} M) of the two compounds were prepared in methanol. Absorption spectra were recorded in the wavelength range from 190 to 500 nm. The absorption of light starts at around 400 nm. For compound **1**, absorption maxima were located at 221, 247, 272, 294 and 321 nm. Compound **2** had absorption maxima at 211, 241, 260, 277, 294 and 338 nm (Figure 3).

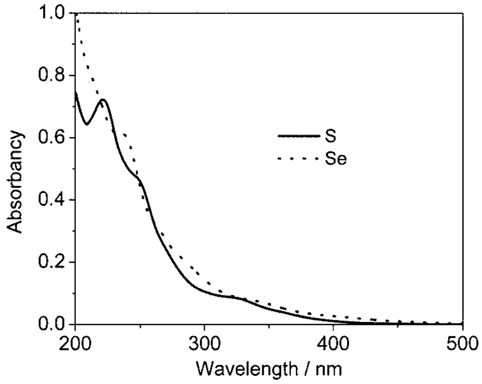

Figure 3. Absorption spectra of $[Re_6S_7O(3,5\text{-}Me_2PzH)_6]Br_2\cdot3,5\text{-}Me_2PzH$ (**1**) and $[Re_6Se_7O(3,5\text{-}Me_2PzH)_6]Br_2\cdot3,5\text{-}Me_2PzH$ (**2**)

For excitation of the luminescence, a Nd:YAG laser with fourth harmonic generation (266 nm) was used. To avoid destruction of the compound, the applied laser energy was set to be less than 300 μJ per pulse. The emission spectra were recorded in the wavelength range 560−785 nm. For both compounds broad emission spectra were found. The light emission of **2** was shifted about 30 nm to the red, relative to **1**. Figure 4 shows the emission spectra of the two compounds in methanol solution. Both emission spectra were fitted with two Gaussian peaks (Table 1). For the determination of the fluorescence decay constants, the fluorescence intensity was integrated in the wavelength range from 560 to 785 nm. The resulting fluorescence decay as a function of the increasing time between the laser pulse and the detection of the fluorescence is shown in Figure 5. The derived fluorescence decay times are summarised in Table 1. For compound **1**, the longer fluorescence decay time corresponds to 84.0% of the fluorescence intensity at time $t = 0$, and for compound **2** to 72.5%. Compound **2** shows a somewhat longer fluorescence decay time than **1**. However, the two Gaussian emission distributions found for each compound do not show any remarkable difference in their fluorescence decay behaviour.

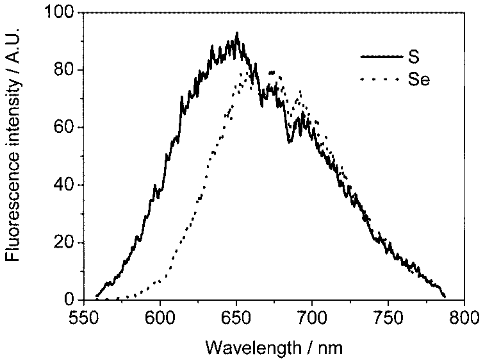

Figure 4. Emission spectra of $[Re_6S_7O(3,5\text{-}Me_2PzH)_6]Br_2\cdot3,5\text{-}Me_2PzH$ (**1**) and $[Re_6Se_7O(3,5\text{-}Me_2PzH)_6]Br_2\cdot3,5\text{-}Me_2PzH$ (**2**) in methanol

Table 1. Fluorescence spectroscopic data

Compound	Fluorescence decay time [µs]/ Fluorescence emission maxima [nm]	
1	0.61±0.06/632.4 (49%)	3.07±0.03/692.8 (51%)
2	0.49±0.02/650.0 (24%)	3.96±0.02/688.3 (76%)

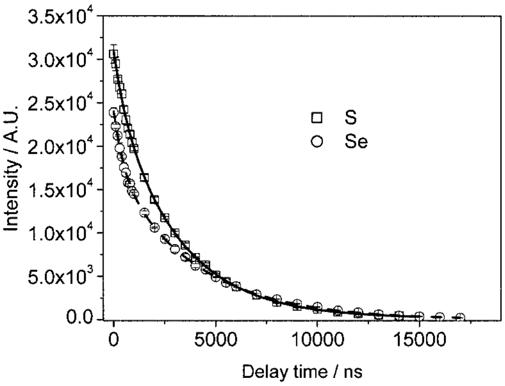

Figure 5. Fluorescence decay of $[Re_6S_7O(3,5\text{-}Me_2PzH)_6]Br_2{\cdot}3,5\text{-}Me_2PzH$ (**1**) and $[Re_6Se_7O(3,5\text{-}Me_2PzH)_6]Br_2{\cdot}3,5\text{-}Me_2PzH$ (**2**) in methanol

The emissive properties of these clusters could be used in photodynamic therapy. This phenomenon will be the subject of our future investigations.

Thermal Properties

Studying the thermal stability of both compounds in vacuo showed that the release of 3,5-dimethylpyrazole ligands begins near 200 °C; decomposition with complete removal of 7 mol-equiv. of 3,5-Me_2PzH is finished at 330 °C; however, it is not possible to mark out separate steps of mass loss on the TG curve.

Conclusion

An original method for the synthesis of organic−inorganic rhenium cluster compounds has been demonstrated using the molten organic ligand 3,5-dimethylpyrazole as the reaction medium for the replacement of the apical bromide atoms in the cluster core. Two new octahedral rhenium cluster complexes, having the composition $[Re_6S_7O(3,5\text{-}Me_2PzH)_6]Br_2{\cdot}3,5\text{-}Me_2PzH$ and $[Re_6Se_7O(3,5\text{-}Me_2PzH)_6]Br_2{\cdot}3,5\text{-}Me_2PzH$, were synthesised in a high yield and their structures have been solved and refined. An interesting feature of the chemistry of these compounds is the unexpected ligand exchange in the octahedral cluster core $\{Re_6(\mu_3\text{-}Q_7Br)\}^{3+}$, namely the replacement of the inner μ_3-Br^- ligand by an oxygen ion O^{2-}, which results in the formation of the cluster core $\{Re_6(\mu_3\text{-}Q_7O)\}^{2+}$. Such a substitution is rather unusual in the chemistry of octahedral clusters. The cluster compounds investigated show promising spectroscopic and photophysical properties. The great variety of organic ligands grafting on the cluster core offers abundant opportunities to modify the spectroscopic and photophysical properties, and the organic shell can make the cluster molecule bioavailable. In this nexus, coupling of target-seeking biomolecules to the cluster moiety seems to be an interesting line of future research. Such organic−inorganic hybrids have great inherent potential as diagnostically and therapeutically relevant compounds.

Experimental Section

Materials and Syntheses: All reagents were used as purchased. $Cs_3[Re_6(\mu_3\text{-}Se_7Br)Br_6]{\cdot}H_2O$ was prepared as described.[22] $Cs_3[Re_6(\mu_3\text{-}S_7Br)Br_6]{\cdot}H_2O$ was synthesised similarly. Microanalyses for C, H, N, S were performed at the Laboratory of Microanalysis of Vorozhtsov Institute of Organic Chemistry, Siberian Branch RAS with a Vario EL from Elementar Analysensysteme GmbH. FTIR: Bruker IFS-85, Perkin−Elmer 1760X. UV/Vis spectra were recorded in methanol solution with a Cary 5G spectrophotometer (Varian). Emission spectra of these solutions were obtained by use of time-resolved laser-induced fluorescence spectroscopy (TRLFS). The setup is described elsewhere.[25] For excitation, a diode-pumped Nd:YAG laser with fourth harmonic generation (266 nm) was used (DIVA II; Soliton). The repetition rate was 20 Hz and the energy of the laser was set to be 300 µJ per pulse. Thermal properties were studied using Thermoanalyser TA-7000 in vacuo in the temperature interval 25−500 °C with a rate of about 10 K/min.

$[Re_6S_7O(3,5\text{-}Me_2PzH)_6]Br_2{\cdot}3,5\text{-}Me_2PzH$ (1) and $[Re_6Se_7O(3,5\text{-}Me_2PzH)_6]Br_2{\cdot}3,5\text{-}Me_2PzH$ (2): Synthetic procedures for both compounds were analogous. Crystals, suitable for X-ray structure determination, were separated manually from the reaction mixture. For preparation of **1**, $Cs_3Re_6S_7Br_7{\cdot}H_2O$ (0.2 g, 0.0863 mmol) and 3,5-dimethylpyrazole (0.2 g, 2.08 mmol) were heated in a sealed glass ampoule at 200 °C for 2 d. The ampoule was cooled at a rate of about 20 °C/h, then the excess of dimethylpyrazole was removed by washing with diethyl ether. CsBr, formed during the reaction, was removed by washing with water. Yield 95% (180 mg, 0.0819 mmol). Compound **2** was prepared in the same way: $Cs_3Re_6Se_7Br_7{\cdot}H_2O$ (0.2 g, 0.0756 mmol) was heated with 3,5-dimethylpyrazole (0.2 g, 2.08 mmol). Yield: 93% (177 mg, 0.0703 mmol). $C_{35}H_{56}Br_2N_{14}ORe_6S_7$ (**1**) (2190.44): calcd. C 19.2, H 2.6, N 9.0 S, 10.2; found C 19.0, H 2.6, N 8.9, S 10.1. $C_{35}H_{56}Br_2N_{14}ORe_6Se_7$ (**2**) (2518.68): calcd. C 16.7, H 2.2, N 7.8; found C 16.8, H 2.1, N 7.7. The IR spectra (400−4000 cm^{-1}) of **1** and **2** show all the peaks expected for 3,5-Me_2PzH. In the spectrum of **1** the peak at 415 cm^{-1} was assigned to Re−(μ_3-S) vibration.

Structure Determination: Single-crystal X-ray diffraction data were collected with the use of graphite-monochromatised Mo-K_α radiation (λ = 0.71073 Å) at 293 K with a Bruker SMART diffractometer, equipped with a CCD area detector. The structures were solved by direct methods using SHELXS-90[23] and refined with SHELXL-97.[24] An empirical absorption correction (Ψ-scan) was applied. All non-hydrogen atoms were refined anisotropically. In both structures there are 65 crystallographically independent non-hydrogen atoms which reside at general positions. The positions of hydrogen atoms were calculated corresponding to their geometrical conditions and refined using the riding model. CCDC-231769 (**1**) and -231770 (**2**) contain the supplementary 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.

1: Orange block, crystal dimensions 0.03 × 0.04 × 0.04 mm, orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 11.4967(7)$ Å, $b = 14.7903(9)$ Å, $c = 32.109(2)$ Å, $V = 5459.8(6)$ Å^3 ($T = 293(2)$ K), $\rho_{\text{calcd.}} = 2.664$ g cm^{-1}, $\mu = 15.02$ mm^{-1}, 23730 measured reflections, 7849 independent ($R_{\text{int}} = 0.0561$), $R(F) = 0.0332$ for 7166 reflections with $F_{hkl} \geq 4\sigma(F_{hkl})$ and $R_w(F^2) = 0.0742$ for all independent reflections. The absolute structure was established by use of the Flack parameter, which is close to 0.

2: Orange block, crystal dimensions 0.03 × 0.045 × 0.055 mm, orthorhombic, space group $P2_12_12_1$, $Z = 4$, $a = 11.473(4)$ Å, $b = 14.885(5)$ Å, $c = 32.902(12)$ Å, and $V = 5619(3)$ Å^3 [$T = 293(2)$ K], $\rho_{\text{calcd.}} = 2.977$ g cm^{-1}, $\mu = 18.872$ mm^{-1}, 33397 measured reflections, 12747 independent ($R_{\text{int}} = 0.1355$), $R(F) = 0.0669$ for 9338 reflections with $F_{hkl} \geq 4\sigma(F_{hkl})$ and $R_w(F^2) = 0.1693$ for all independent reflections. The absolute structure was established by use of the Flack parameter, which is close to 0.

Acknowledgments

This research was supported by INTAS (grant 00-00689) and by the Sächsisches Staatsministerium für Wissenschaft und Kunst, Aktenzeichen: 4-7531.50-04-844-03/7. The authors thank also the DLR Internationales Büro des BMBF (WTZ Project RUS 01/241) for support.

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Received June 3, 2004