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Cluster Core Controlled Reactions of Substitution of Terminal Bromide Ligands by Triphenylphosphine in Octahedral Rhenium Chalcobromide Complexes

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Abstract: Reactions of rhenium chalcobromides $Cs_4[\{Re_6(\mu_3\text{-}S)_8\}Br_6]\cdot 2H_2O$, $Cs_3[\{Re_6(\mu_3\text{-}Se)_8\}Br_6]\cdot 2H_2O$, $Cs_3[\{Re_6(\mu_3\text{-}Q)_7(\mu_3\text{-}Br)\}Br_6]\cdot H_2O$ (Q = S, Se), and $K_2[\{Re_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2\}Br_6]$ with molten triphenylphosphine (PPh_3) have resulted in a family of novel molecular hybrid inorganic–organic cluster compounds. Six octahedral rhenium cluster complexes containing PPh_3 ligands with general formula $[\{Re_6(\mu_3\text{-}Q)_{8-n}(\mu_3\text{-}Br)_n\}(PPh_3)_{4-n}Br_{n+2}]$ (Q = S, n = 0, 1, 2; Q = Se, n = 0, 1) have been synthesized and characterized by X-ray single-crystal diffraction and elemental analyses, $^{31}P\{^1H\}$ NMR, luminescent measurements, and quantum-chemical calculations. It was found that the number of terminal PPh_3 ligands in the complexes is controlled by the composition and consequently by the charge of the cluster core $\{Re_6Q_{8-n}Br_n\}^{n+2}$. In crystal structures of the complexes with mixed chalcogen/bromine ligands in the cluster core all positions of a cube $[Q_{8-n}Br_n]$ are ordered and occupied exclusively by Q or Br atoms. Luminescence characteristics of the compounds *trans*-$[\{Re_6Q_8\}(PPh_3)_4Br_2]$ and *fac*-$[\{Re_6Se_7Br\}(PPh_3)_3Br_3]$ (Q = S, Se) have been investigated in CH_2Cl_2 solution and the broad emission spectra in the range of 600–850 nm were observed.

Introduction

Hexanuclear rhenium(III) cluster complexes of general formula $[\{Re_6Q_8\}L_6]$, where Q is μ_3-chalcogenide ligands (S, Se, or Te) and L− inorganic acido ligands or organic species are the subject of extensive current studies. Heightened attention to these complexes is due to their structural, redox, and photoluminescent properties as well as a rich chemistry which descends from a versatility of the coordination environment of the octahedral cluster core $\{Re_6(\mu_3\text{-}Q)_8\}$. Present interest is focused on clusters coordinated by organic N- and P-donor ligands.[1–4] Such inorganic–organic hybrids show interesting structural, electronic, and optical properties. The main strategy in their preparation is the substitution of terminal ligands L that can be controlled with respect to the number of the ligands substituted and their geometrical arrangement around the cluster core. The first representatives of the Re_6 cluster complexes with PEt_3 and CH_3CN terminal ligands have been obtained in solution starting from the corresponding oxidized Re_6 chalcohalide compounds.[5,6] Another effective way for preparation of complexes with terminal organic ligands is the use of the proper molten organic compounds as a reaction media. Recently this approach was used for preparation of cuboidal clusters of molybdenum and tungsten with diphosphine terminal ligands[7] and of octahedral rhenium cluster complexes with 3,5-dimethylpyrazole as terminal ligands (3,5-Me_2pzH).[8,9] By the examples of octahedral rhenium cluster complexes with 3,5-Me_2pzH ligands we have shown that, in contrast to ligand substitution reactions in solutions, both oxidized and nonoxidized Re_6 chalcohalide cluster anions can be involved in direct ligand substitution with organic ligands in their melt. Here we have exploited this methodology with the use of molten triphenylphosphine as reaction media for the synthesis of rhenium cluster complexes with terminal PPh_3 ligands. Included in the present investigation is the study of the influence of precursor cluster core composition on the stoichiometry and structure of

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(1) Gabriel, J. C. P.; Boubekeur, K.; Uriel, S.; Batail, P. *Chem. Rev.* **2001**, *101*, 2037–2066.
(2) Selby, H. D.; Roland, B. K.; Zheng, Z. *Acc. Chem. Res.* **2003**, *36*, 933–944.
(3) Selby, H. D.; Roland, B. K.; Cole, J. R.; Zheng, Z. P. *Macromol. Symp.* **2004**, *209*, 23–39.
(4) Selby, H. D.; Zheng, Z. P. *Comments Inorg. Chem.* **2005**, *26*, 75–102.

(5) Zheng, Z. P.; Long, J. R.; Holm, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 2163–2171.
(6) Willer, M. W.; Long, J. R.; McLauchlan, C. C.; Holm, R. H. *Inorg. Chem.* **1998**, *37*, 328–333.
(7) Feliz, M.; Llusar, R.; Uriel, S.; Vicent, C.; Humphrey, M. G.; Lucas, N. T.; Samoc, M.; Luther-Davies, B. *Inorg. Chim. Acta* **2003**, *349*, 69–77.
(8) Mironov, Y. V.; Shestopalov, M. A.; Brylev, K. A.; Yarovoi, S. S.; Romanenko, G. V.; Fedorov, V. E.; Spies, H.; Pietzsch, H. J.; Stephan, H.; Geipel, G.; Bernhard, G.; Kraus, W. *Eur. J. Inorg. Chem.* **2005**, 657–661.
(9) Mironov, Y. V.; Brylev, K. A.; Shestopalov, M. A.; Yarovoi, S. S.; Fedorov, V. E.; Spies, H.; Pietzsch, H. J.; Stephan, H.; Geipel, G.; Bernhard, G.; Kraus, W. *Inorg. Chim. Acta* **2006**, *359*, 1129–1134.

the compounds formed. Most of previous research has been focused on the use of cluster complexes with chalcogenide cluster cores, $\{Re_6S_8\}$ and $\{Re_6Se_8\}$, as starting compounds. In the present work we report the syntheses, crystal and electronic structures, and luminescent properties of the series of complexes: *trans*-[$\{Re_6(\mu_3\text{-}Q)_8\}(PPh_3)_4Br_2$] (Q = S (**1**), Se (**2**)), *fac*-[$\{Re_6(\mu_3\text{-}Q)_7(\mu_3\text{-}Br)\}(PPh_3)_3Br_3$] (Q = S (**3**), Se (**4**)), *cis*-[$\{Re_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2\}(PPh_3)_2Br_4$] (**5**), and *trans*-[$\{Re_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br_2)\}(PPh_3)_2Br_4$]·$4H_2O$ (**6**) with both chalcogenide $\{Re_6Q_8\}$ and mixed-ligand chalcobromide $\{Re_6Q_{8-n}Br_n\}$ (n = 1, 2) cluster cores.

Experimental Section

Materials and Synthesis. $Cs_4[Re_6S_8Br_6]$·$2H_2O$, $Cs_3[Re_6Se_8Br_6]$·$2H_2O$, $Cs_3[Re_6Q_7Br_7]$·H_2O (Q = S, Se), and $K_2[Re_6S_6Br_8]$ were synthesized as described previously.[10–13] All other reagents were used as purchased.

Elemental analyses for C, H, and S (Carlo Erba 1106) were performed in the Laboratory of Microanalysis of the Institute of Organic Chemistry, Novosibirsk. Energy dispersive spectroscopy (EDS) was performed on an EDAX equipped (JEOL EX-23000BU) JEOL JSM-6700F field emission scanning electron microscope. Infrared spectra were measured on KBr pellets with a Bruker IFS-85 Fourier spectrometer. The $^{31}P\{^1H\}$ NMR spectra of CD_2Cl_2 solutions were recorded at 20 °C on the Bruker CXP-300 spectrometer (57.2 MHz) using HP detectors. X-ray powder diffraction data were collected on a Philips APD 1700 instrument. The thermal properties were studied on Derivatograph Q-1500 MOM (Hungary) in the temperature range 25–500 °C.

General Procedure for Syntheses of Compounds 1–4. A 100 mg amount of proper Re_6 cluster compound and an excess of PPh_3 (100 mg) were heated in sealed glass tube at 200 °C for 2 days. The reaction mixture was cooled to room temperature with the rate of 10 °C/h. The product of reaction was washed by ether for removing PPh_3 excess and by water to dissolve CsBr formed in the reaction. Yields: 103 mg (98%) (**1**); 108 mg (95%) (**2**); 102 mg (93%) (**3**); 104 mg (97%) (**4**). Single crystals for X-ray structural analyses were separated manually from the reaction mixtures. Anal. Calcd. for $C_{72}H_{60}Br_2P_4Re_6S_8$ (**1**): C, 33.48; H, 2.34; S, 9.93. Found: C, 33.25; H, 2.26; S, 9.87. Anal. Calcd for $C_{72}H_{60}Br_2P_4Re_6Se_8$ (**2**): C, 29.24; H, 2.04. Found: C, 28.99; H, 2.08. Anal. Calcd for $C_{54}H_{45}Br_4P_3Re_6S_7$ (**3**): C, 26.49; H, 1.85; S, 9.17. Found: C, 26.21; H, 2.08; S, 9.12. Anal. Calcd for $C_{54}H_{45}Br_4P_3Re_6Se_7$ (**4**): C, 23.36; H, 1.63. Found: C, 23.07; H, 1.52. EDS shows the following: Re:S:Br:P ratio of 6:7.7:1.9:4.2 for $C_{72}H_{60}Br_2P_4Re_6S_8$ (**1**); Re:Se:Br:P ratio of 6:8.1:1.8:4.3 for $C_{72}H_{60}Br_2P_4Re_6Se_8$ (**2**), Re:S:Br:P ratio of 6:6.8:4.1:3.3 for $C_{54}H_{45}Br_4P_3Re_6S_7$ (**3**); Re:Se:Br:P ratio of 6:7.1:4.2:2.9 for $C_{54}H_{45}Br_4P_3Re_6Se_7$ (**4**). In $^{31}P\{^1H\}$ NMR spectra of **1–6** only one signal is observed: δ −25.4 for **1**; δ −22.5 for **2**; δ −10.4 for **3**; δ −18.2 for **4**; δ −11.0 for **5**; δ −6.4 for **6**. IR spectra (400−4000 cm^{-1}) of compounds **1–6** show all peaks expected for PPh_3. In spectra of compounds **1**, **3**, **5**, and **6** the bands at 416, 420, 418, and 417 cm^{-1} correspondingly may be assigned to Re−(μ_3-S) vibration. X-ray powder patterns of the compounds **1–6** are in good agreement with the data calculated on the basis of the results of the single-crystal study.

Synthesis of Compounds 5 and 6. $K_2Re_6S_6Br_8$ (200 mg, 0.099 mmol) and PPh_3 (200 mg, 0.76 mmol) were heated in the sealed glass tube at 200 °C for 2 days. The reaction mixture was cooled to room temperature with the rate of 10 °C/h. The product was extracted from the reaction mixture by three portions (10 mL) of CH_2Cl_2 to give a dark red solution. The solution was chromatographed on a silica gel column. Fraction 1 (CH_2Cl_2, R_f = 0.97), orange band: **5**. Red crystals were obtained by slow evaporation of solution at room temperature in air. Yield: 56 mg (24.6%). Anal. Calcd for $C_{36}H_{30}Br_6P_2Re_6S_6$ (**5**): C, 18.69; H, 1.31; S, 8.32. Found: C, 18.37; H, 1.78; S, 8.31. EDS: Re: S:Br:P ratio is 6:5.8:5.9:2. Fraction 2 (CH_2Cl_2, R_f = 0.82), orange band: **3**. Yield: 24 mg (9.9%). Fraction 3 (CH_2Cl_2, R_f = 0.51) orange band: **6**. Red crystals were obtained by slow evaporation of solution at room temperature in air. Yield: 120 mg (51.8%). Anal. Calcd for $C_{36}H_{38}Br_6O_4P_2Re_6S_6$ (**6**): C, 18.12; H, 1.60; S, 8.07. Found: C, 18.41; H, 1.56; S, 8.16. EDS: Re:S:Br:P ratio is 6:5.8:6.1:2.1. Fraction 4 (Me$_2$-CO), brown band: unknown admixture.

Crystallography. Single-crystal X-ray diffraction data were collected with the use of graphite monochromatized Mo Kα radiation (λ = 0.71073 Å) at 293 K on a Bruker Nonius X8Apex diffractometer equipped with a 4K CCD area detector. The φ-scan technique was employed to measure intensities. Absorption corrections were applied using the SADABS program.[14,15] The crystal structures were solved independently by direct methods and were refined by full-matrix least-squares techniques with the use of the SHELX package.[16] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the water molecules in compound **4** were not located. The positions of hydrogen atoms of PPh_3 ligands were calculated corresponding to their geometrical conditions and refined using the riding model. Crystallographic data as well as details of data collection and refinement for complexes **1–6** are given in Table 1 and in the Supporting Information. Table 2 tabulates some metrical details for the present compounds. CCDC 620891−620896 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.

Luminescent Measurements. The compounds *trans*-[$\{Re_6S_8\}(PPh_3)_4$-Br$_2$] (**1**), *trans*-[$\{Re_6Se_8\}(PPh_3)_4Br_2$] (**2**), *fac*-[$\{Re_6S_7Br\}(PPh_3)_3Br_3$] (**3**), and *fac*-[$\{Re_6Se_7Br\}(PPh_3)_3Br_3$] (**4**) were dissolved in CH_2Cl_2. The final concentration of the compounds in the solvent was about 10^{-4} M. The solutions were measured in a 1 cm fluorescence cuvette (Helma, Germany).

These solutions were studied by time-resolved laser-induced fluorescence spectroscopy. To excite the luminescence, a Nd:YAG laser system (Inlite, Continnum Corp. USA) was used. The fundamental output of the laser was two times frequency doubled to achieve a laser wavelength of 266 nm. The repetition rate of the laser was set to be 20 Hz, and the pulse energy, applied to the samples, was attenuated to be about 5 mJ/pulse. The luminescence emission was focused into an optical fiber, and the spectrum was resolved in a 275 mm spectrograph (Acton Research). The measurement of the spectrum was performed by an intensified CCD camera system (Roper Scientific) with 1024 × 1024 pixels. The settings of the intensifier are as follows: gain, 128; gate width, 20 μs; and 100 accumulations on CCD. Each spectrum was recorded 3 times. The time resolution was 500 ns, and the delay range was from 0 to 20 μs.

Computational Details. Spin-restricted density functional calculations (DFT) were carried out on models with general formula [$\{Re_6$-(μ_3-Q)$_{8-n}(\mu_3$-Br)$_n\}]Br_{n+2}$] and [$\{Re_6(\mu_3$-Q)$_{8-n}(\mu_3$-Br)$_n\}(PH_3)_{4-n}Br_{n+2}$] (Q = S, n = 0, 1, 2; Q = Se, n = 0, 1) using the ADF2003 code.[17] The PPh$_3$ groups were substituted by the PH$_3$ groups for ease of calculations. The procedure of full optimization was used. The local-exchange VWN correlation potential was used for the local density (LDA) approxima-

(10) Yarovoi, S. S.; Solodovnikov, S. F.; Mironov, Y. V.; Fedorov, V. E. *J. Struct. Chem. (Engl. Transl.)* **2003**, *44*, 318−321.
(11) Yarovoi, S. S.; Mironov, Y. V.; Naumov, D. Y.; Gatilov, Y. V.; Kozlova, S. G.; Kim, S. J.; Fedorov, V. E. *Eur. J. Inorg. Chem.* **2005**, 3945−3949.
(12) Yarovoi, S. S.; Mironov, Y. V.; Solodovnikov, S. F.; Virovets, A. V.; Fedorov, V. E. *Mater. Res. Bull.* **1999**, *34*, 1345−1351.
(13) Slougui, A.; Ferron, S.; Perrin, A.; Sergent, M. *J. Cluster Sci.* **1997**, *8*, 349−359.

(14) *APEX2*, Version 1.08; *SAINT*, Version 7.03; Bruker Advanced X-ray Solutions, Bruker AXS Inc.: Madison, WI, 2004.
(15) *SADABS*, Version 2.11; Bruker Advanced X-ray Solutions, Bruker AXS Inc.: Madison, WI, 2004.
(16) *SHELXTL*, Version 6.12; Bruker Advanced X-ray Solutions, Bruker AXS Inc.: Madison, WI, 2004.
(17) *Amsterdam Density Functional (ADF) Program*, Release 2003; Vrije Universiteit: Amsterdam, The Netherlands, 2003.

Table 1. Crystal Data and Structure Refinements for **1−6**

	1	2	3	4	5	6
empirical formula	$C_{72}H_{60}Br_2P_4Re_6S_8$	$C_{72}H_{60}Br_2P_4Re_6Se_8$	$C_{54}H_{45}Br_4P_3Re_6S_7$	$C_{54}H_{45}Br_4P_3Re_6Se_7$	$C_{36}H_{30}Br_6P_2Re_6S_6$	$C_{36}H_{38}Br_6O_4P_2Re_6S_6$
fw	2582.58	2957.78	2448.07	2776.37	2313.56	2385.62
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/m$	$P\bar{1}$
a (Å)	12.4001(3)	12.3444(2)	11.6455(3)	11.6642(16)	10.302(2)	10.2225(6)
b (Å)	16.1927(4)	16.2377(4)	14.8271(4)	14.880(2)	20.292(4)	11.5987(7)
c (Å)	19.1937(5)	19.5427(4)	20.1655(5)	20.446(4)	12.108(2)	12.5588(6)
α (deg)			76.738(1)	77.159(5)		83.651(2)
β (deg)	101.780(1)	102.103(1)	74.951(1)	75.012(4)	105.38(3)	74.953(2)
γ (deg)			67.853(1)	67.931(5)		75.664(2)
V (Å³)	3772.75(16)	3830.16(14)	3080.60(14)	3145.7(8)	2440.5(9)	1391.53(13)
Z	2	2	2	2	2	1
ρ_{calc} (g/cm³)	2.273	2.565	2.639	2.931	3.148	2.847
μ (cm⁻¹)	109.93	144.11	146.86	181.99	200.81	176.19
cryst size (mm)	0.20 × 0.20 × 0.10	0.30 × 0.07 × 0.02	0.18 × 0.10 × 0.08	0.19 × 0.13 × 0.13	0.20 × 0.08 × 0.05	0.08 × 0.06 × 0.02
T_{min}; T_{max}	0.1278; 0.3338	0.3101; 0.7515	0.1774; 0.3862	0.130; 0.201	0.118; 0.403	0.2910; 0.7010
θ range, deg	2.20−26.37	2.73−29.43	3.17−25.68	3.10−25.68	2.31−25.88	2.53−27.18
reflecns collected	27 083	28 140	21 113	21 371	12 764	9796
unique reflecns	7705	6797	11 182	11 404	4626	4843
R_{int}	0.0297	0.0408	0.0215	0.0241	0.1789	0.0357
param refined	415	415	559	559	229	265
$R_1(F)$ [$F_o^2 > 2\sigma(F_o^2)$]	0.0303	0.0321	0.0313	0.0341	0.0700	0.0537
$R_w(F^2)$ (all data)	0.0790	0.0798	0.0947	0.1025	0.1934	0.1764

Table 2. Selected Bond Lengths (Å) for **1−6**

compound	Re−Re, Å	Re−μ_3-Q, Å	Re−μ_3-Br, Å	Re−Br$_{terminal}$, Å	Re−P, Å
1	2.5884(3)−2.5972(3)	2.381(2)−2.413(2)		2.5471(7)	2.517(2)−2.522(2)
2	2.6284(4)−2.6542(4)	2.5013(7)−2.5267(7)		2.5672(7)	2.515(2)−2.522(2)
3	2.5823(4)−2.6268(4)	2.383(2)−2.469(2)	2.5867(9)−2.595(1)	2.5191(9)−2.5445(9)	2.497(2)−2.515(2)
4	2.6122(6)−2.6577(6)	2.4888(9)−2.5282(9)	2.6105(9)−2.619(1)	2.538(1)−2.564(1)	2.504(2)−2.525(2)
5	2.595(2)−2.658(3)	2.410(7)−2.487(6)	2.615(5)−2.637(4)	2.507(3)−2.535(4)	2.509(7)
6	2.5844(9)−2.6302(9)	2.430(4)−2.459(4)	2.578(2)−2.594(2)	2.511(2)−2.516(2)	2.511(4)

Table 3. Calculated Atomic Charges in the Model Complexes $[\{Re_6(\mu_3\text{-}Q)_{8-n}(\mu_3\text{-Br})_n\}Br_{n+2}]$ and $[\{Re_6(\mu_3\text{-}Q)_{8-n}(\mu_3\text{-Br})_n\}(PH_3)_{4-n}Br_{n+2}]$ (Q = S, n = 0, 1, 2; Q = Se, n = 0, 1)

	cluster core atoms[a]			ligands[a]	
model complexes	Re	Q	Br	Br	P
trans-[{Re₆S₈}Br₂]	0.12 (2), 0.16 (4)	−0.07 (8)		−0.17 (2)	
trans-[{Re₆S₈}(PH₃)₄Br₂]	0.09 (2), 0.03 (4)	−0.10 (8)		−0.17 (2)	0.19 (4)
trans-[{Re₆Se₈}Br₂]	0.09 (2), 0.11 (4)	−0.03 (8)		−0.20 (2)	
trans-[{Re₆Se₈}(PH₃)₄Br₂]	0.06 (2), 0.01 (4)	−0.04 (8)		−0.29(2)	0.17 (4)
fac-[{Re₆S₇Br}Br₃]	0.11 (3), 0.16 (3)	−0.04 (3), −0.05 (3), −0.10 (1)	0.11 (1)	−0.18 (3)	
fac-[{Re₆S₇Br}(PH₃)₃Br₃]	0.03 (3), 0.10 (3)	−0.07 (3), −0.08 (3), −0.12 (1)	0.10 (1)	−0.23 (3)	0.19 (3)
fac-[{Re₆Se₇Br}Br₃]	0.08 (3), 0.11 (3)	0.00 (6), −0.06 (1)	0.11 (1)	−0.21 (3)	
fac-[{Re₆Se₇Br}(PH₃)₃Br₃]	0.01 (3), 0.07 (3)	−0.01 (3), −0.03 (3), −0.06 (1)	0.10 (1)	−0.26 (3)	0.17 (3)
cis-[{Re₆S₆Br₂}Br₄]	0.16 (2), 0.11 (4)	−0.03 (4), −0.05 (2)	0.10 (2)	−0.18 (2), −0.19 (2)	
cis-[{Re₆S₆Br₂}(PH₃)₂Br₄]	0.04 (2), 0.10 (4)	−0.05 (4), −0.06 (2)	0.09 (2)	−0.21 (2), −0.22 (2)	0.20 (2)
trans-[{Re₆S₆Br₂}Br₄]	0.15 (2), 0.11 (4)	−0.03 (4), −0.04 (2)	0.10 (2)	−0.18 (4)	
trans-[{Re₆S₆Br₂}(PH₃)₂Br₄]	0.04 (2), 0.10 (4)	−0.05 (4), −0.06 (2)	0.08 (2)	−0.22 (4)	0.20 (2)

[a] Number of corresponding atoms is shown in parentheses.

tion,[18] Becke's nonlocal corrections to the exchange energy[19] and Perdew's nonlocal corrections to the correlation energy were added.[20] The ZORA (zero-order relativistic approximation) method was used to account for the scalar relativistic effects.[21] The STO basic set without core potentials was used for all atoms (ZORA/TZ2P). The atomic net charges for several $[\{Re_6(\mu_3\text{-}Q)_{8-n}(\mu_3\text{-Br})_n\}Br_{n+2}]$ and $[\{Re_6(\mu_3\text{-}Q)_{8-n}(\mu_3\text{-Br})_n\}(PH_3)_{4-n}Br_{n+2}]$ (Q = S, n = 0, 1, 2; Q = Se, n = 0, 1) models presented in Table 3 are obtained using the Hirshfeld analysis.[22]

A special feature of charge calculations is that the group PH₃ (it may be that the PPh₃ too) influences on the symmetry negligibly because the symmetry of charge distribution is conserved for [{Re₆-

(18) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200−1211.
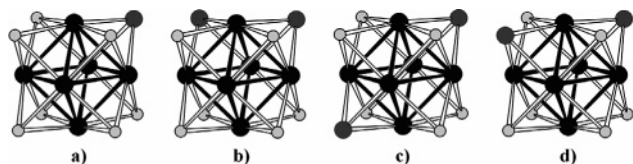(19) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−100.
(20) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822−8824.
(21) van Lenthe, E.; Ehlers, A.; Baerends, E. J. *J. Chem. Phys.* **1999**, *110*, 8943−8953.
(22) Hirshfeld, F. L. *Theor. Chim. Acta* **1977**, *44*, 129−38.

$(\mu_3\text{-}Q)_{8-n}(\mu_3\text{-Br})_n\}Br_{n+2}]$ and $[\{Re_6(\mu_3\text{-}Q)_{8-n}(\mu_3\text{-Br})_n\}(PH_3)_{4-n}Br_{n+2}]$ models with a precision of two decimal places (Table 3).

Also the bonding energies for all three possible isomeric forms of $[Re_6Q_6Br_8]^{2-}$ (Q = S, Se) and atomic net charges on Re atoms for starting complexes $[\{Re_6Q_7Br\}Br_6]^{3-}$ and $[\{Re_6S_6Br_2\}Br_6]^{2-}$ were calculated (see Discussion and the Supporting Information).

Results

Syntheses. Six new octahedral rhenium cluster compounds, namely, *trans*-[{Re₆(μ_3-Q)₈}(PPh₃)₄Br₂] (Q = S (**1**), Se (**2**)), *fac*-[{Re₆(μ_3-Q)₇(μ_3-Br)}(PPh₃)₃Br₃] (Q = S (**3**), Se (**4**)), *cis*-[{Re₆(μ_3-S)₆(μ_3-Br)₂}(PPh₃)₂Br₄] (**5**), and *trans*-[{Re₆(μ_3-S)₆-(μ_3-Br)₂}(PPh₃)₂Br₄]·4H₂O (**6**) have been prepared by the reactions of the corresponding ionic chalcobromide complexes Cs₄[{Re₆(μ_3-S)₈}Br₆]·2H₂O, Cs₃[{Re₆(μ_3-Se)₈}Br₆]·2H₂O, Cs₃-

Figure 1. Structure of the cluster core $\{Re_6Q_7Br\}$ (a) and three possible isomers of cluster core $\{Re_6Q_6Br_2\}$ (b−d).

$[\{Re_6(\mu_3\text{-}Q)_7(\mu_3\text{-}Br)\}Br_6]\cdot H_2O$ (Q = S, Se), and $K_2[\{Re_6(\mu_3\text{-}S)_6(\mu_3\text{-}Br)_2\}Br_6]$ with molten PPh$_3$. All compounds obtained in these reactions are molecular complexes. They are stable in air and do not decompose in inert atmosphere (He) up to 200 (for **3**−**6**) and 350 °C (for **1** and **2**). For the separation of different isomers, column chromatography was employed. In the case of the $\{Re_6S_6Br_2\}$ cluster core, two isomers of the three possible ones were isolated (Figure 1b−d).

All obtained compounds are 24e clusters with the Re atoms in the +3 oxidation state, even in the case of use of the oxidized complex $[\{Re_6Se_8\}Br_6]^{3-}$ as precursor. This is not surprising, because it was shown earlier that the reactions involving substitution of terminal halogen ligands in 23e cluster complexes $[\{Re_6Q_8\}L_6]^{3-}$ (L = Cl, Br, I) by organic ligands as a rule are accompanied by the spontaneous one-electron reduction of the cluster.[5,6,9,23−27]

It is interesting to note that the composition of the compounds synthesized strongly depends on the charge of the cluster core $\{Re_6Q_{8-n}Br_n\}^{n+2}$ in the starting cluster complexes. These results differ from the previously described reactions of chalcobromide octahedral rhenium cluster complexes with 3,5-dimethylpyrazol, where all six terminal Br ligands were substituted by organic molecules.[8,9]

The formation of octahedral cluster complexes with PPh$_3$ as terminal ligands is known for some transition metals. Recently, several examples of neutral complexes with cluster cores $\{M_6Q_8\}$ coordinated by six PPh$_3$ ligands were described, for example, $[Ru_6Se_8(PPh_3)_6]$,[28] $[W_6S_8(PPh_3)_6]$,[29] and $[Co_6Q_8\text{-}(PPh_3)_6]$ (Q = S, Se).[30,31] The majority of studies on Re$_6$ complexes with phosphine ligands were carried out with PEt$_3$.[1,2,5,23,32] There are three examples of structurally characterized Re$_6$ complexes containing PPh$_3$ ligand, namely, *cis*-[Re$_6$-Se$_8$(PPh$_3$)$_2$(4,4′-dipyridyl)$_2$](SbF$_6$)$_2$ and its derivatives: $[\{Re_6\text{-}Se_8(PPh_3)_4(4,4'\text{-}dipyridyl)_2\}_2\{Cd(NO_3)_2\}](SbF_6)_4\cdot 21C_4H_{10}O\cdot 21CH_2Cl_2$ and $[\{Re_6Se_8(PPh_3)_4(4,4'\text{-}dipyridyl)_2\}\text{-}\{Cd(NO_3)_3\}](NO_3)\cdot 2C_4H_{10}O\cdot CH_2Cl_2$.[33] In addition, the compounds *fac*-[Re$_6$Se$_8$(PPh$_3$)$_3$(isonicotinamide)$_3$](SbF$_6$)$_2$, *fac*-[Re$_6$-Se$_8$(PPh$_3$)$_3$(MeCN)$_3$](SbF$_6$)$_2$, and *cis*-[Re$_6$Se$_8$(PPh$_3$)$_4$(MeCN)$_2$]-
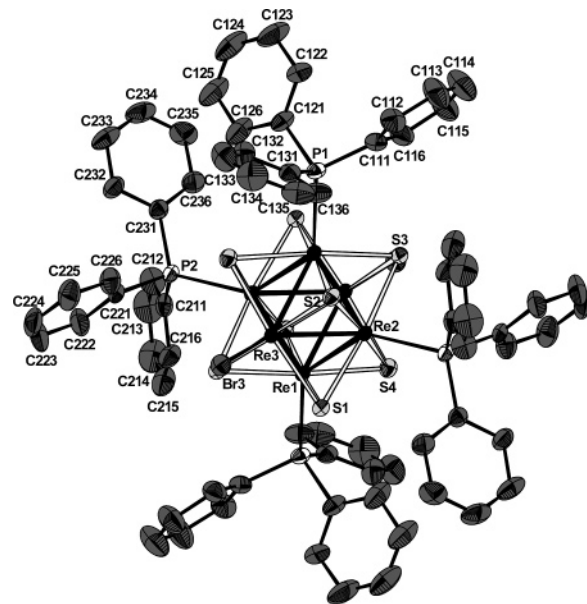
Figure 2. Structure of *trans*-[$\{Re_6S_8\}(PPh_3)_4Br_2$] in **1**. Displacement ellipsoids of the non-hydrogen atoms are drawn at the 30% probability level. H atoms of the PPh$_3$ ligands have been omitted for clarity.

(SbF$_6$)$_2$ were reviewed by Zheng et al.[3,4] Also some related complexes with phosphine derivatives are known: [Re$_6$Se$_8$-(MePPh$_2$)$_6$](SbF$_6$)$_2\cdot$2H$_2$O, [Re$_6$Se$_8$((Me$_2$TTF)PPh$_2$)$_6$](SbF$_6$)$_2$, and [Re$_6$Se$_8$(FcPPh$_2$)$_6$](SbF$_6$)$_2\cdot$5CH$_2$Cl$_2$.[34]

Structures. All compounds obtained were characterized by single-crystal X-ray diffraction analysis. The most interesting feature of these solids with mixed-ligand cluster cores is the formation of crystal structures without disorder in the cluster core. In the known Re$_6$ cluster complexes with a mixed chalcohalide cluster core $\{Re_6Q_{8-n}X_n\}$ as a rule each corner of the cube [$Q_{8-n}X_n$] is occupied statistically by Q and X atoms. There is only one example of a compound with an ordered mixed-ligand cluster core—*cis*-[$\{Re_6Te_6Cl_2\}(TeCl_2)_2Cl_4$],[35] where the structure of the cluster core is similar to that found in *cis*-[$\{Re_6S_6Br_2\}(PPh_3)_2Br_4$] (**5**).

trans-[$\{Re_6S_8\}(PPh_3)_4Br_2$] (1) and *trans*-[$\{Re_6Se_8\}(PPh_3)$-$_4Br_2$] (2). Compounds **1** and **2** are isostructural and were obtained only in one isomeric form, as *trans*-isomers. The cluster cores in **1** and **2** contain a Re$_6$ octahedron residing inside a Q$_8$ cube (Q = S, Se). Re−Re and Re−Q distances are typical for 24e Re$_6$ complexes, and their geometrical details do not differ significantly from the starting material and related compounds. Four Re atoms in the equatorial plane are coordinated by PPh$_3$ molecules and the two remaining Re atoms in *trans*-positions are coordinated by Br ligands. The structure of molecule **1** is shown in Figure 2. Compound **2** has a similar structure. All atoms in the structures **1** and **2** are located in general positions. The unit cell contains three rhenium and four chalcogen atoms that are crystallographically independent, all of which belong to the same cluster core. The centers of the clusters coincide with the centrosymmetrical special crystallographic position (0, $^1/_2$, 0; $^1/_2$, $^1/_2$, $^1/_2$). There are not any notable interactions between molecules in the crystal structures. The Re−Re, Re−Q, Re−P, and the Re−Br distances are tabulated in Table 2.

(23) Zheng, Z. P.; Gray, T. G.; Holm, R. H. *Inorg. Chem.* **1999**, *38*, 4888−4895.
(24) Yoshimura, T.; Umakoshi, K.; Sasaki, Y.; Sykes, A. G. *Inorg. Chem.* **1999**, *38*, 5557−5564.
(25) Yoshimura, T.; Umakoshi, K.; Sasaki, Y.; Ishizaka, S.; Kim, H. B.; Kitamura, N. *Inorg. Chem.* **2000**, *39*, 1765−1772.
(26) Chen, Z. N.; Yoshimura, T.; Abe, M.; Sasaki, Y.; Ishizaka, S.; Kim, H. B.; Kitamura, N. *Angew. Chem., Int. Ed.* **2001**, *40*, 239−242.
(27) Chen, Z. N.; Yoshimura, T.; Abe, M.; Tsuge, K.; Sasaki, Y.; Ishizaka, S.; Kim, H. B.; Kitamura, N. *Chem. Eur. J.* **2001**, *7*, 4447−4455.
(28) Eckermann, A. L.; Wunder, M.; Fenske, D.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **2002**, *41*, 2004−2006.
(29) Jin, S.; Zhou, R.; Scheuer, E. M.; Adamchuk, J.; Rayburn, L. L.; DiSalvo, F. J. *Inorg. Chem.* **2001**, *40*, 2666−2674.
(30) Hong, M.; Huang, Z.; Lei, X.; Wei, G.; Kang, B.; Liu, H. *Inorg. Chim. Acta* **1989**, *159*, 1−2.
(31) Hong, M.; Huang, Z.; Lei, X.; Wei, G.; Kang, B.; Liu, H. *Polyhedron* **1991**, *10*, 927−34.
(32) Zheng, Z. P.; Holm, R. H. *Inorg. Chem.* **1997**, *36*, 5173−5178.
(33) Selby, H. D.; Orto, P.; Carducci, M. D.; Zheng, Z. P. *Inorg. Chem.* **2002**, *41*, 6175−6177.

(34) Perruchas, S.; Avarvari, N.; Rondeau, D.; Levillain, E.; Batail, P. *Inorg. Chem.* **2005**, *44*, 3459−3465.
(35) Mironov, Y. V.; Pell, M. A.; Ibers, J. A. *Inorg. Chem.* **1996**, *35*, 2709−2710.
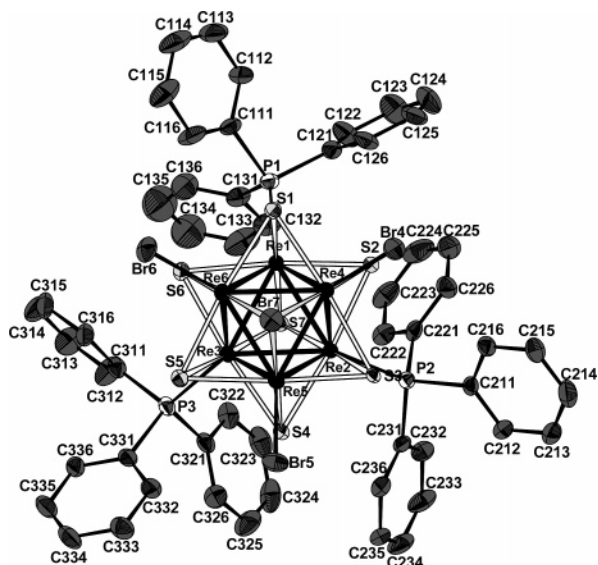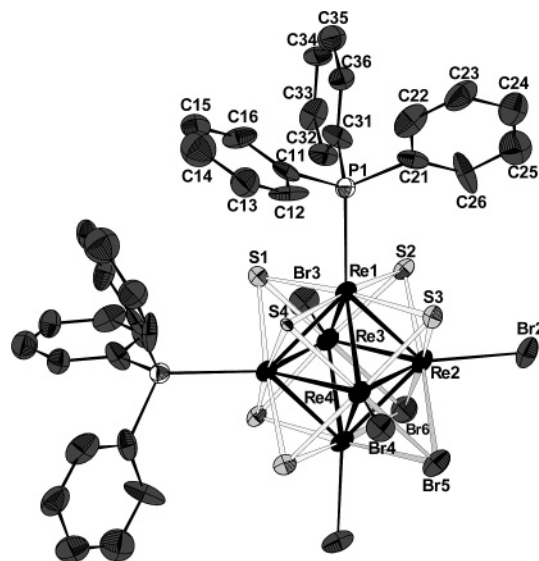
Figure 3. Structure of *fac*-[{Re$_6$S$_7$Br}(PPh$_3$)$_3$Br$_3$] in **3**. Displacement ellipsoids of the non-hydrogen atoms are drawn at the 30% probability level. H atoms of the PPh$_3$ ligands have been omitted for clarity.
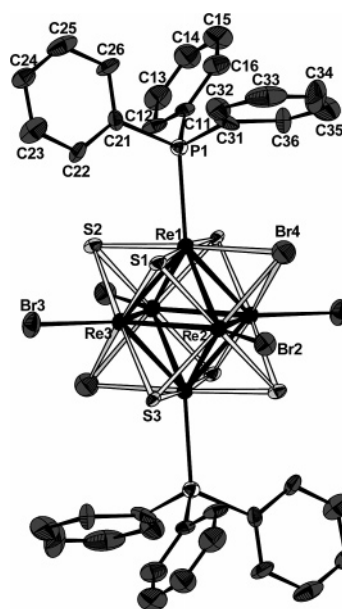

Figure 4. Structure of *cis*-[{Re$_6$S$_6$Br$_2$}(PPh$_3$)$_2$Br$_4$] in **5**. Displacement ellipsoids of the non-hydrogen atoms are drawn at the 30% probability level. H atoms of the PPh$_3$ ligands are not shown.

fac-[{Re$_6$S$_7$Br}(PPh$_3$)$_3$Br$_3$] (3) and *fac*-[{Re$_6$Se$_7$Br}(PPh$_3$)$_3$-Br$_3$] (4). The compounds **3** and **4** are isostructural. All atoms and centers of the cluster cores are located in general positions. Each cluster core is built from six rhenium, one bromine, and seven chalcogen atoms that are crystallographically independent. The cluster cores {Re$_6$Q$_7$Br} contain a pseudocube [Q$_7$Br] (Figure 1a). There is no atom disorder in the cluster core: seven positions are occupied only by S in **3** or Se in **4** and one position is occupied by a bromine atom. Three Re atoms of the same face are coordinated by PPh$_3$ ligands, and three remaining Re are coordinated by Br atoms forming a *fac*-isomer. The μ_3-Br atom occupies only one position in the cluster core and is connected to three Re atoms bonded with terminal Br ligands. The structure of molecule **3** is shown in Figure 3; **4** has a similar structure. There are no remarkable interactions between the molecular complexes *fac*-[{Re$_6$Q$_7$Br}(PPh$_3$)$_3$Br$_3$] in crystal structures **3** and **4**. The Re–Re, Re–Q, Re–μ_3-Br, Re–P, and the Re–Br$_{terminal}$ distances are presented in Table 2. The Re–μ_3-Br distances for octahedral rhenium cluster complexes with mixed-ligand cluster cores were not presented previously because of disorder in such compounds.

cis-[{Re$_6$S$_6$Br$_2$}(PPh$_3$)$_2$Br$_4$] (5). In this compound six corners of the [S$_6$Br$_2$] cube are occupied exclusively by S atoms. The two other corners of the cube, which lie on the edge of cube (Figure 1b), are occupied exclusively by Br atoms. The four Re atoms that are bonded to μ_3-Br ligands have terminal Br ligands (Figure 4). The unit cell contains one crystallographically independent cluster unit. The Re3, Re4, S1, S4, Br5 and Br6 (μ_3-ligands), and Br3 and Br4 (terminal ligands) atoms lay on the mirror plane (x, $^1/_4$, z) that bisects the molecule. All other atoms are located in general positions. The Re–Re, Re–S, Re–μ_3-Br, Re–P, and the Re–Br$_{terminal}$ distances are shown in Table 2. There are no noticeable interactions between the molecules in the crystal structure.

trans-[{Re$_6$S$_6$Br$_2$}(PPh$_3$)$_2$Br$_4$]·4H$_2$O (6). In this compound two Br atoms occupy the body diagonal of the cube [S$_6$Br$_2$] (Figure 1c). Four Re atoms in a equatorial plane are coordinated by Br atoms, and the two remaining Re atoms are coordinated by PPh$_3$ molecules to form the *trans*-isomer (Figure 5). The


Figure 5. Structure of *trans*-[{Re$_6$S$_6$Br$_2$}(PPh$_3$)$_2$Br$_4$] in **6.** Displacement ellipsoids of the non-hydrogen atoms are drawn at the 30% probability level. H atoms of the PPh$_3$ ligands have been omitted for clarity.

cluster core is built from three rhenium, three sulfur, and one bromine atom, all of which are crystallographically independent. All atoms are located in general positions, while the center of the cluster coincides with the special crystallographic position ($^1/_2$, 0, $^1/_2$). The Re–Re, Re–S, Re–μ_3-Br, Re–P, and the Re–Br$_{terminal}$ distances are listed in Table 2. The cluster units do not interact with each other. The water molecules are connected in pairs by weak hydrogen bonds (the O⋯O distance is 2.87 Å) and the pairs are linked via hydrogen bonding to the μ_3-Br atoms (the O⋯Br distance is 3.45 Å) (Figure 6).

Luminescent Properties. The luminescent properties of CH$_2$-Cl$_2$ solutions of compounds **1**–**4** were studied. Compound **1** shows a broad luminescence emission in the wavelength range from 600 to 850 nm, with a maximum at about 725 nm. The luminescence decay is found to be monoexponential with a decay time of 5.6 ± 0.1 μs. The compound **3** shows almost no
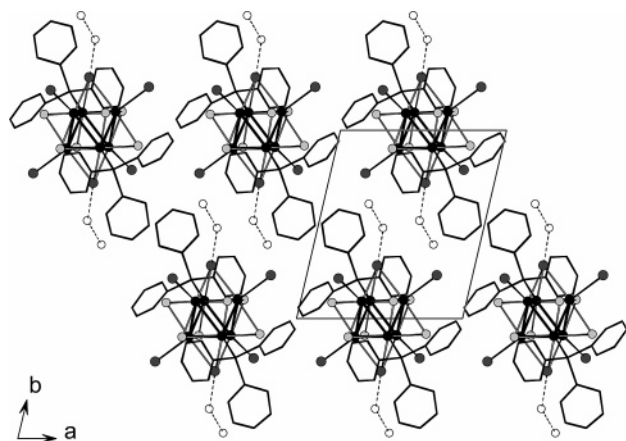
Figure 6. Hydrogen bonding interactions (indicated by dashed lines) between crystallization water molecules and μ_3-Br ligands of cluster complex in **6** (view down [001]). H atoms of the PPh$_3$ ligands and water molecules have been omitted.
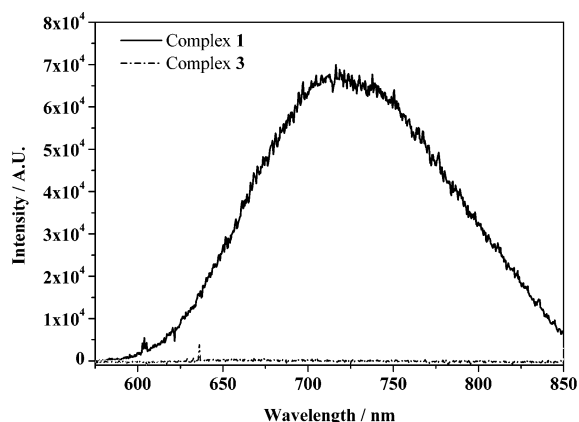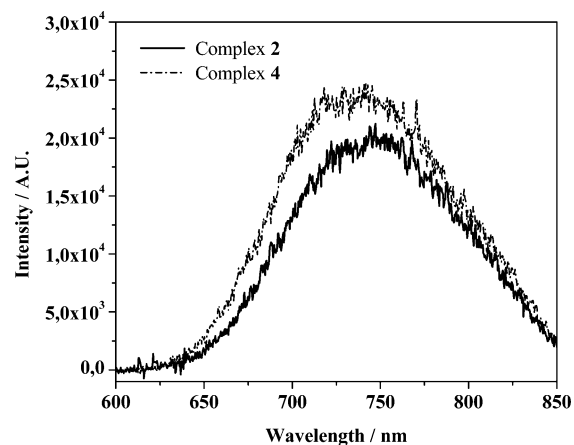

Figure 7. Luminescence spectra of *trans*-[{Re$_6$S$_8$}(PPh$_3$)$_4$Br$_2$] (**1**) and *fac*-[{Re$_6$S$_7$Br}(PPh$_3$)$_3$Br$_3$] (**3**).

luminescence. The maximum of the residual luminescence is located at about 740 nm, and the decay time could not be determined. At the moment there is no explanation for this behavior. The luminescence spectra are shown in Figure 7.

The selenium-containing compounds show a completely different behavior. Both compounds **2** and **4** show luminescence spectra with nearly the same intensity at comparable delay time. The spectra are shown in Figure 8. The emission maxima are located at about 745 nm for **2** and 738 nm for **4**. The luminescence decay times are determined to be 3.2 ± 0.1 and 0.95 ± 0.05 μs for **2** and **4,** respectively. The dependences of the integrated luminescence intensities as a function of the delay time for compounds **1**, **2**, and **4** are shown in Figure 9.

The negative intensities at high delay times for **2** and **4** are a result of temperature problems in cooling of the CCD camera chip, giving too high of a background correction. Compared to the sulfur-containing compound **1**, the selenium-containing compounds show somewhat lower luminescence intensities.

In contrast to the recently published data for [{Re$_6$Q$_7$O}(3,5-Me$_2$pzH)$_6$]Br$_2$·3,5-Me$_2$pzH and [{Re$_6$Q$_8$}(3,5-Me$_2$pzH)$_6$]Br$_2$·2(3,5-Me$_2$pzH) (Q = S, Se),[8,9] the compounds described here have only monoexponential luminescence decay. The decay times are of the same order of magnitude (microseconds). The maxima of the luminescence for the new compounds are shifted to longer wavelength.

Figure 8. Luminescence spectra of *trans*-[{Re$_6$Se$_8$}(PPh$_3$)$_4$Br$_2$] (**2**) and *fac*-[{Re$_6$Se$_7$Br}(PPh$_3$)$_3$Br$_3$] (**4**).
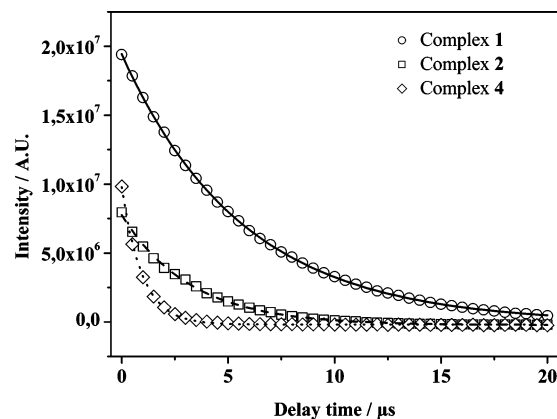
Figure 9. Luminescence decay behavior of the compounds **1**, **2**, and **4**.
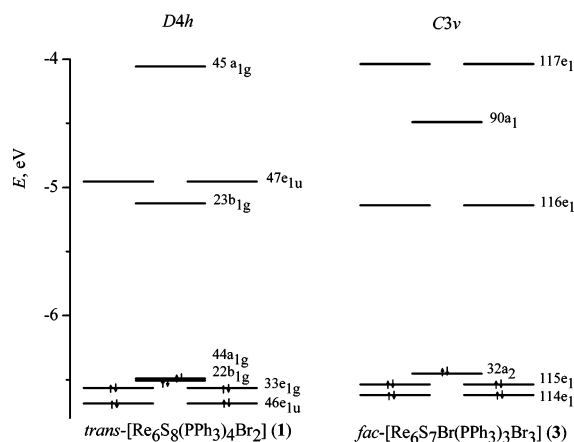
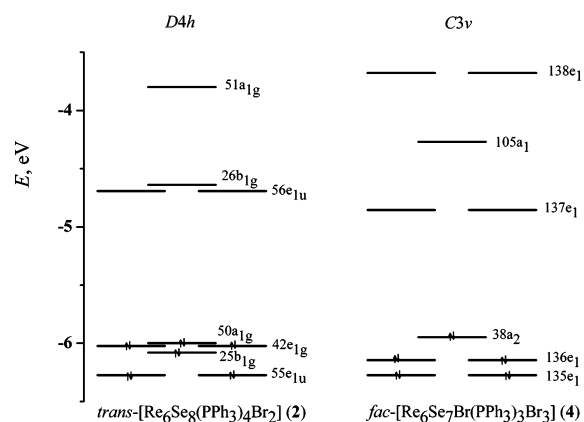**Figure 10.** DFT energy level diagram for complexes *trans*-[{Re$_6$S$_8$}(PPh$_3$)$_4$-Br$_2$] (**1**) and *fac*-[{Re$_6$S$_7$Br}(PPh$_3$)$_3$Br$_3$] (**3**) in the symmetries with the approximation described in the text.

The long-lived emission is accounted for by symmetry- and spin-forbidden transitions between the HOMO and LUMO in the [{Re$_6$Q$_8$}X$_6$]$^{4-}$ (Q = S, Se and X = Cl, Br, and I) complexes.[36,37] The complexes are different in symmetry, which demonstrates the role of cluster symmetry on luminescent properties (Figures 10−12). For example, complexes **3** and **4** have the C_{3v} symmetry (ignoring PPh$_3$ influence) and the
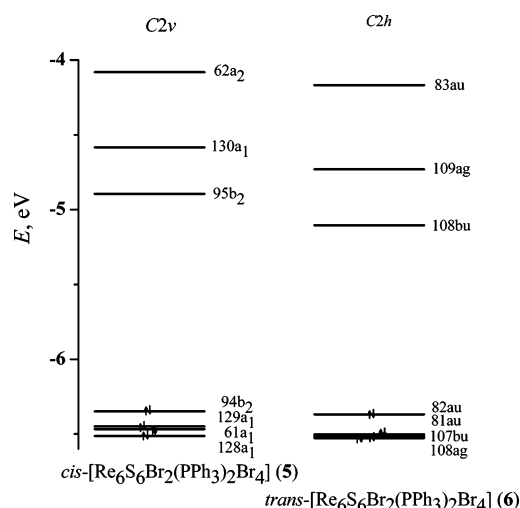
(36) Gray, T. G.; Rudzinski, C. M.; Meyer, E. E.; Holm, R. H.; Nocera, D. G. *J. Am. Chem. Soc.* **2003**, *125*, 4755−4770.
(37) Gray, T. G.; Rudzinski, C. M.; Meyer, E. E.; Nocera, D. G. *J. Phys. Chem. A* **2004**, *108*, 3238−3243.

Figure 11. DFT energy level diagram for complexes *trans*-[{Re₆-Se₈}(PPh₃)₄Br₂] (**2**) and *fac*-[{Re₆Se₇Br}(PPh₃)₃Br₃] (**4**) in the symmetries with the approximation described in the text.

Figure 12. DFT energy level diagram for for complexes *cis*-[{Re₆S₆-Br₂}(PPh₃)₂Br₄] (**5**) and *trans*-[{Re₆S₆Br₂}(PPh₃)₂Br₄] (**6**) in the symmetries with the approximation described in the text.

electron−dipole transitions between the HOMO and LUMO (32a₂ ↔ 116e₁ and 38a₂ ↔137e₁) are allowed. Experimentally the decreasing of luminescence decay time for complex **4** and practically the absence of luminescence effects for complex **3** are observed. Complexes **1** and **2** have D_{4h} symmetry (ignoring PPh₃ influence also). The electron−dipole transitions are forbidden between the HOMO and LUMO (44a₁g ↔ 23b₁g) in complex **1** and for this complex the greatest decay time is observed. The lowest unoccupied orbitals 56e₁u and 26b₁g have an energy separation of 0.05 eV in complex **2**. It is difficult to predict which one of these two orbitals is the LUMO. The electron−dipole transitions are allowed between 50a₁g ↔ 56e₁u and forbidden between 50a₁g ↔ 26b₁g. In this case an intermediate value of the luminescence decay time is observed (Figure 9).

Apparently, the existence of symmetry-forbidden transitions increases the lifetime of emission. Hence one would expect a decrease of lifetime for *cis*-[{Re₆S₆Br₂}(PPh₃)₂Br₄] (**5**) complexes. The nature of luminescence kinetic processes is certainly much more complicated[36−38] than the qualitative explanation proposed in our discussion. Moreover, we do not take into account spin−orbital interactions, which principally should be

considered.[39−43] However, we believe that the approach presented here for analysis of cluster core symmetry would allow the purposeful control of the luminescence lifetime.

³¹P{¹H} NMR Spectra. In every ³¹P{¹H} NMR spectrum of compounds **1**−**6** one signal is observed. This result is in good agreement with the structural data: the signals can be assigned to only one isomeric form, namely, *trans*-[{Re₆Q₈}(PPh₃)₄Br₂] (for **1** and **2**), *fac*-[{Re₆Q₇Br}(PPh₃)₃Br₃] (for **3** and **4**), *cis*-[{Re₆Q₆Br₂}(PPh₃)₂Br₄] (for **5**), or *trans*-[{Re₆Q₆Br₂}(PPh₃)₂-Br₄] (for **6**). The most negative chemical shift values correspond to the compounds with the shortest average Re−P distances. This dependence can be explained by an increase of electron density on the P atoms due to the back-donation from the 5d orbitals of the Re atoms. The chemical shift values decrease in the following series: **3** (δ −10.4) < **5** (δ −11.0) < **4** (δ −18.2) < **2** (δ −22.5) < **1** (δ −25.4), while the average Re−P distances increase in the same sequence (2.507 Å (**3**) < 2.509 Å (**5**) < 2.513 Å (**4**) < 2.518 Å (**2**) < 2.520 Å (**1**)). Only the *trans*-[{Re₆Q₆Br₂}(PPh₃)₂Br₄] complex (**6**) does not follow this trend (δ −6.4; 2.511 Å).

Discussion

The series of octahedral rhenium cluster complexes with cluster cores {Re₆Q₈₋ₙBrₙ}$^{n+2}$ (Q = S, Se; n = 0, 1, 2) and terminal PPh₃ ligands were prepared using molten triphenylphosphine as reaction medium. Additionally, solution chemistry permitted isolation of different isomers.

Reactions of the anionic cluster complexes [{Re₆S₈}Br₆]⁴⁻, [{Re₆S₈}Br₆]³⁻, [{Re₆Q₇Br}Br₆]³⁻ (Q = S, Se), and [{Re₆S₆Br₂}-Br₆]²⁻ with molten PPh₃ lead to the formation of the complexes with mixed Br/PPh₃ terminal ligands. The original compositions of the cluster cores in these reactions remain inalterable. In such complexes an octahedral Re₆ cluster is inscribed into a pseudocube [Q₈₋ₙBrₙ] of eight µ₃-ligands. According to the previous ⁷⁷Se NMR study of (PPh₄)₂[Re₆Se₆Br₈],[44] for the cluster core {Re₆Se₆Br₂} all three possible isomeric units were found with the ratio (%) of isomers **b**:**c**:**d** = 27:61:12 (Figure 1). An interesting feature of **c** in comparison with the other two isomers is the fact that all Re atoms in the cluster core in **c** are equivalent: they have the same ligand environment and, consequently, equal atomic charges (see Supporting Information).

The calculated bonding energy values of [{Re₆Se₆Br₂}Br₆]²⁻ isomers (−116.18 for **b** (C_{2v} symmetry), −116.26 for **c** (D_{3d}), and −116.03 eV for **d** (C_{2v})) are in good agreement with the distribution of isomers determined by ⁷⁷Se NMR data. The bonding energy values of [{Re₆S₆Br₂}Br₆]²⁻ isomers have the same regularity (−120.57 for **b**, −120.65 for **c**, and −120.40 eV for **d**). Thus, the ⁷⁷Se NMR and the bonding energy values for isomers of [{Re₆Q₆Br₂}Br₆]²⁻ (Q = S, Se) suggest that the ratio of isomers in system [Re₆S₆Br₈]²⁻ is similar to the selenium

(38) Kitamura, N.; Ueda, Y.; Ishizaka, S.; Yamada, K.; Aniya, M.; Sasaki, Y. *Inorg. Chem.* **2005**, *44*, 6308−6313.

(39) Arratia-Perez, R.; Hernandez-Acevedo, L. *J. Chem. Phys.* **1999**, *110*, 2529−2532.

(40) Arratia-Perez, R.; Hernandez-Acevedo, L. *J. Chem. Phys.* **1999**, *111*, 168−172.

(41) Alvarez-Thon, L.; Hernandez-Acevedo, L.; Arratia-Perez, R. *J. Chem. Phys.* **2001**, *115*, 726−730.

(42) Arratia-Perez, R.; Hernandez-Acevedo, L. *J. Chem. Phys.* **2003**, *118*, 7425−7430.

(43) Hernandez-Acevedo, L.; Arratia-Perez, R. *J. Chil. Chem. Soc.* **2003**, *48*, 125−128.

(44) Yarovoi, S. S.; Solodovnikov, S. F.; Tkachev, S. V.; Mironov, Y. V.; Fedorov, V. E. *Russ. Chem. Bull.* **2003**, *52*, 68−72.

Scheme 1. Charge Distribution on Rhenium Atoms According to DTF Calculations[a]
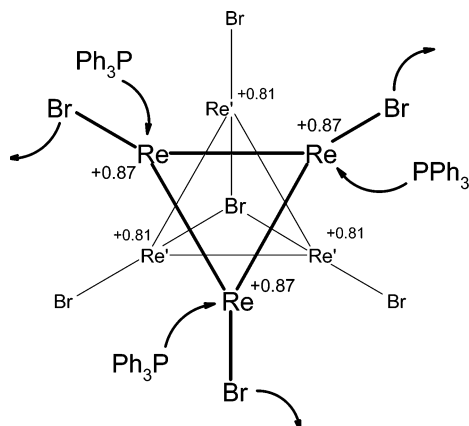
[a] Bold lines correspond to the upper part of octahedral complex [{Re$_6$S$_7$Br}Br$_6$]$^{3-}$. supposed scheme of substitution of terminal Br ligands by PPh$_3$ is indicated by arrows. Sulfur atoms are omitted for clarity.

analogue. This hypothesis is in agreement with the yields of compounds **5** and **6**. The low content of the third isomer **d** did not allow us to isolate it from the reaction mixture.

In this work the reactivity of the octahedral rhenium cluster chalcobromide complexes with three types of cluster cores, namely, {Re$_6$Q$_8$}, {Re$_6$Q$_7$Br}, and {Re$_6$S$_6$Br$_2$}, have been studied. The isolation of two isomeric compounds containing {Re$_6$S$_6$Br$_2$} cluster cores was successful. All compounds synthesized are molecular complexes. It was estimated that in the conditions studied the number of neutral terminal PPh$_3$ ligands depends on the composition of the cluster core. The Re−L (L = Br$_{terminal}$, PPh$_3$) distances depend on a nature of the chalcogen atoms: selenium containing compounds have longer Re−L average distances than their sulfur analogues (Table 2). For all compounds the Re−L distances are in a good agreement with literature data.[10,12,13,33] This is the main difference from the compounds containing 3,5-Me$_2$pzH ligands where all six terminal ligands were substituted by organic molecules.[8,9] It was also shown earlier that reactions between mixed-ligand cluster complexes [{Re$_6$Q$_7$Br}Br$_6$]$^{3-}$ (Q = S, Se) and molten 3,5-Me$_2$pzH resulted in substitution of μ_3-Br ligand in the cluster core by oxygen with formation of cationic cluster complexes [{Re^{6}Q$_7$O}(3,5-Me$_2$pzH)$_6$]$^{2+}$ [8] in addition to substitution of terminal bromine ligands by molecules of 3,5-Me$_2$pzH.

Only one other example of a Re$_6$ cluster complex with ordered arrangement of the μ_3 ligands in mixed-ligand chalcohalide cluster core has been reported to date, *cis*-[{Re$_6$Te$_6$Cl$_2$}(TeCl$_2$)$_2$-Cl$_4$].[35] It is interesting to note that the TeCl$_2$ ligands are coordinated to the Re atoms that are bonded only by μ_3-Te ligands. Our new compounds make a good addition to the family of octahedral rhenium clusters with an atomic ordering in the cluster core.

We believe that the atomic ordering in the cluster core is controlled by the preference by PPh$_3$ ligands to coordinate with rhenium atoms which are bonded exclusively with μ_3-Q atoms (Q = S, Se) as seen in the structures of compounds described here. DFT calculations of rhenium atomic charges in mixed-ligand chalcobromide complexes used as starting compounds confirm our hypothesis (see the table in the Supporting Information). For example, in the cluster anion [{Re$_6$S$_7$Br}Br$_6$]$^{3-}$

the rhenium atoms coordinated by a μ_3-Br atom have less positive charge than the atoms coordinated only by a μ_3-S (Scheme 1). Apparently, PPh$_3$ as a nucleophilic agent prefers to coordinate to Re atoms with a more positive charge.

Using an excess of triphenylphosphine in reactions with cluster chalcobromides, we expected the substitution of all terminal ligands in the starting compounds and the formation of complexes with six terminal PPh$_3$ ligands (as it was found in the similar reactions with the melt of excess of 3,5-dimethylpyrazole[8,9]). However, the compounds obtained here have only four (**1** and **2**), three (**3** and **4**), or even two (**5** and **6**) terminal PPh$_3$ ligands. Such results may be explained by the preferred formation of neutral molecular compounds with the general formula [{Re$_6$(μ_3-Q)$_{8-n}$(μ_3-Br)$_n$}(PPh$_3$)$_{4-n}$Br$_{n+2}$] (Q = S, n = 0, 1, 2; Q = Se, n = 0, 1).

In the literature some related molecular rhenium cluster complexes with PPh$_2$(CH$_2$)$_6$PPh$_2$ (dpph), PPh$_2$CH$_2$PPh$_2$ (dppm), PPh$_2$(CH$_2$)$_2$POPh$_2$ (dppeO), PPh$_2$(CH$_2$)$_4$POPh$_2$ (dppbO), and PEt$_3$ ligands are described. The structures of compounds *trans*-[Re$_6$Se$_8$(μ_2-dpph)$_2$I$_2$];[26] *trans*-[Re$_6$Se$_8$I$_2$(η^1-dppm)$_4$], *trans*-[Re$_6$-Se$_8$I$_2$(η^1-dppeO)$_4$], and *trans*-[Re$_6$Se$_8$I$_2$(η^1-dppbO)$_4$];[27] and *trans*-[Re$_6$Se$_8$(PEt$_3$)$_4$I$_2$][5] are similar to those found in compounds **1** and **2**. Every dpph ligand in the complex *trans*-[Re$_6$Se$_8$(μ_2-dpph)$_2$I$_2$] is coordinated to two neighboring Re atoms of the same cluster in a bridge-chelate manner, whereas dppm, dppeO, dppbO, and PEt$_3$ ligands in corresponding complexes are monodentate. Organic P-donor ligands in these complexes are coordinated to four Re atoms in the equatorial plane of the rhenium octahedron. Two remaining Re atoms in trans-positions are coordinated by iodine atoms.

In conclusion, six novel octahedral rhenium cluster complexes with the general formula [{Re$_6$(μ_3-Q)$_{8-n}$(μ_3-Br)$_n$}(PPh$_3$)$_{4-n}$-Br$_{n+2}$] (Q = S, n = 0, 1, 2; Q = Se, n = 0, 1) have been synthesized by reaction of cluster rhenium chalcobromides with molten triphenylphosphine. The compounds were characterized by single-crystal X-ray diffraction and elemental analysis, ^{31}P-{^{1}H} NMR spectroscopy, luminescent measurements, and quantum-chemical calculations. It was shown that compounds **1**, **2**, and **4** exhibit broad emission spectra in the range of 600−850 nm. The interesting feature of structures **3**−**6** is the ligand ordering in mixed chalcohalide cluster cores. By the example of compounds **5** and **6** the possibility of preparation and isolation of isomeric complexes containing cluster cores of composition {Re$_6$S$_6$Br$_2$}$^{4+}$ has been demonstrated.

Supporting Information Available: X-ray crystallographic data (CIF) and a table with calculated rhenium atomic charges in starting complexes [{Re$_6$Q$_7$Br}Br$_6$]$^{3-}$ and [{Re$_6$S$_6$Br$_2$}Br$_6$]$^{2-}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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