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Paramagnetic Triangular Rhenium Sulfide Cluster $[Re_3S_4(Dppe)_3(NCS)_3]Br$

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Abstract—A new cluster $[Re_3S_4(Dppe)_3(NCS)_3]Br$ (Dppe = $Ph_2PCH_2CH_2PPh_2$) is synthesized. The molecular and crystal structures of the cluster are determined by X-ray diffraction analysis. The magnetochemical data indicate the high-spin ground state ($S = 3/2$) of the cluster at room temperature.

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INTRODUCTION

Interest in chalcogenide clusters is explained by their important role in a series of biological and industrial catalytic processes, in particular, in atmospheric nitrogen fixation. New approaches to the preparation of materials based on Mo and W clusters and using redox-active ligands of the dithiolate type have recently been proposed [1]. Similar complexes are considered as one-component molecular conductors with prospects for a combination of the conducting properties with any else ones, for example, magnetic or optical properties [2, 3].

We have recently synthesized $[Re_3S_4(Dppe)_3Br_3]Br$ (**I**) (Dppe = $Ph_2PCH_2CH_2PPh_2$), being the first example of a triangular chalcogenide rhenium cluster with diphosphine ligands [4]. This cluster turned out to be interesting for at least two reasons. First, the high-spin state was detected for this cluster at room temperature (3.87 μ_B), which corresponds to the parallel orientation of spins of three unpaired electrons, and the results of the magnetochemical study were confirmed by the quantum-chemical calculations. Second, the bromide ions coordinated to rhenium turned out to be very mobile, resulting in their partial replacement by chloride ions when the bromide cluster is dissolved in CH_2Cl_2 in the absence of other chloride sources. The obtained mixed-halide complex $[Re_3S_4(Dppe)_3Br_{1.6}Cl_{1.4}]Br$ (**II**) was characterized by X-ray diffraction analysis and mass spectrometry. On the one hand, the high-spin state of the cluster core $[Re_3S_4]^{4+}$ makes it attractive as a building block for the formation of heterospin systems in which the cluster can be bound to the paramagnetic transition metal ions through ambidentate ligands as bridges. On the other hand, it is known that the treatment of $Re_3S_7Br_7$ with a potassium cyanide excess changes the nuclearity of the cluster core and results in the formation of the tetrahedral cluster $[Re_4S_4(CN)_{12}]^{4-}$ [5]. Therefore, it seems necessary to establish whether the $[Re_3S_4]^{4+}$ cluster core remains stable upon the replacement of the terminal halide ions by other anionic ligands and whether its high-spin state is retained or not. This work is devoted to the study of the structure and magnetic properties of the triangular rhenium cluster with the terminal thiocyanate anions: $[Re_3S_4(Dppe)_3(NCS)_3]Br$ (**III**).

EXPERIMENTAL

The synthesis was carried out under argon using the standard Schlenk technique. Compounds **I** and **II** were synthesized according to an earlier described procedure [4]. Solvents for the syntheses were dehydrated and degassed by reflux and distillation under argon using the corresponding drying agents [6]. IR spectra were recorded on a SCIMITAR FTS 2000 instrument. The elemental analyses of the samples to C, H, and N were carried out on a Euro EA 3000 instrument at the Laboratory of Microanalysis of the Nikolaev Institute of Inorganic Chemistry (Siberian Branch, Russian Academy of Sciences).

Synthesis of $[Re_3S_4(Dppe)_3(NCS)_3]Br \cdot 4CH_2Cl_2$ ($III \cdot 4CH_2Cl_2$). Compound **I** (139 mg, 0.063 mmol) and KSCN (69 mg, 0.711 mmol) were placed in a Schlenk flask, and acetonitrile (15 mL) was added. The solution was stirred at room temperature for 24 h. A gray precipitate was filtered off from a red-brown solution, and the filtrate was evaporated in vacuo. The brown residue was dissolved in methylene chloride (5 mL), and diethyl ether (10 mL) was layered onto the obtained solution. After complete mixing, large dark brown crystals suitable for X-ray diffraction analysis were isolated. The yield was 53 mg (34%).

IR (KBr), ν, cm^{-1}: 3050 m, 2909 w, 2049 vs, 1619 w, 1585 w, 1572 w, 1483 m, 1434 s, 1313 w, 1312 w, 1274 w, 1193 w, 1097 m, 1027 w, 999 w, 879 m, 823 m, 741 m, 694 vs, 525 s, 494 m, 419 m.

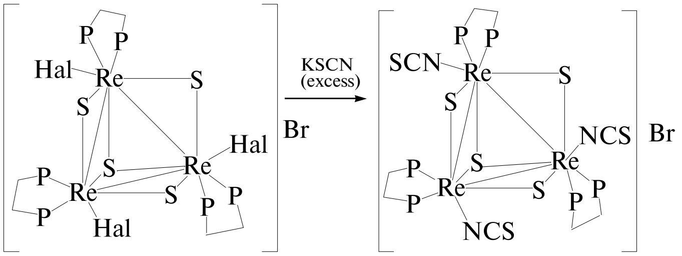
For $C_{81}H_{72}N_3P_6S_7BrRe_3 \cdot 2CH_2Cl_2$[1]

anal. calcd., %:	C, 43.23;	H, 3.32;	N, 1.82.
Found, %:	C, 43.50;	H, 3.25;	N, 1.45.

X-ray diffraction analysis. All measurements were carried out using a standard procedure on a Bruker-Nonius X8 APEX automated four-circle diffractometer (CCD two-coordinate detector, λ = 0.71073 Å, graphite monochromator). Reflections intensities were measured by the φ scan mode of narrow (0.5°) frames to $2\theta_{max} = 52.86°$. An absorption correction was applied empirically (SADABS) [7]. The structure was solved by a direct method and refined by full-matrix least squares in the anisotropic approximation for non-hydrogen atoms (SHELXTL) [7]. Hydrogen atoms were localized geometrically and refined in the rigid body approximation. The crystallographic characteristics of the complexes and X-ray diffraction experimental details are listed in Table 1. Selected interatomic distances are given in Table 2. The crystallographic data were deposited with the Cambridge Crystallographic Data Centre (CCDC no. 946346; http://www.ccdc.cam.ac.uk/conts/retrieving.html) and are available from the authors.

RESULTS AND DISCUSSION

The reactions of chalcogenide clusters **I** or **II** with a KSCN excess in acetonitrile or methanol result in the replacement of the halide ligands by thiocyanate ones and the formation of cluster **III**.



I, Hal = Br
II, Hal = Br/Cl

III

Single crystals of the complex were obtained by the slow diffusion of ether into a solution of **III** in CH_2Cl_2. The X-ray diffraction data indicate that the structure of the cluster cation $[Re_3S_4(Dppe)_3(NCS)_3]^+$ (**III'**) is similar to those of the starting rhenium clusters **I** and **II** (Fig. 1). If the metal–metal bonds are ignored, the environment of each rhenium atom is distorted octahedral. The Re atoms form an almost equilateral triangle, whose Re–Re distances range from 2.7672(3) to 2.7869(3) Å. The replacement of the terminal halide ions by thiocyanate ions exerts nearly no effect on the Re–Re bond lengths (Table 2). As in the case of numerous cationic Mo and W clusters with coordinated diphosphines (e.g., [8–11]), the M–P bonds are somewhat shortened for the phosphorus atoms in the *trans* position to the μ_3-bridging S atom. The same regularity is observed for the M–(μ-S) distances: the longer bonds are observed in the *trans* position to the thiocyanate anions. The average Re–(μ_3-S) and Re–(μ-S) distances in **III** are 2.352(2) and 2.313(17) Å,

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[1] The partial loss of the CH_2Cl_2 solvate molecules was observed during the analysis.

Table 1. Crystallographic characteristics and experimental details for structure **III** · $4CH_2Cl_2$

Parameter	Value
Formula	$C_{85}H_{80}N_3P_6S_7Cl_8BrRe_3$
M	2475.87
Crystal system	Triclinic
Space group	$P\overline{1}$
Temperature, K	150
a, Å	13.7414(4)
b, Å	17.8997(5)
c, Å	18.5937(6)
α, deg	86.764(1)
β, deg	85.753(1)
γ, deg	88.316(1)
V, Å^3	4552.1(2)
Z	2
ρ_{calcd}, g/cm^3	1.806
F(000)	2418
$\mu(MoK_\alpha)$, mm^{-1}	4.96
Crystal size, mm	0.25 × 0.15 × 0.12
θ Range, deg	1.78–26.43
Ranges of reflection indices h, k, l	$-12 \le h \le 17$, $-22 \le k \le 19$, $-23 \le l \le 22$
Number of measured reflections	30141
Number of independent reflections	18378
Number of observed reflections ($I > 2\sigma(I)$)	16108
Number of specified parameters	1018
Number of restraints	98
R_{int}	0.017
$R_1(F^2 > 2\sigma(F^2))$, $wR_2(F^2)$	0.032, 0.087
GOOF	1.08
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	2.65/–1.85

$w = 1/[\sigma^2(F_o^2) + (0.0402P)^2 + 20.8036P]$, $P = (F_o^2 + 2F_c^2)/3$.

respectively. The thiocyanate ligands are coordinated to Re by the nitrogen atoms as in all structurally characterized tetra- and hexanuclear rhenium chalcogenide clusters [12, 13] and in the tri- and tetranuclear tungsten complexes [14–17]. The values of ReNC bond angles range from 164.8(5)° to 169.0(5)°.

All CH_2Cl_2 solvate molecules and bromide anions are localized in the octahedral cavity with the center at (–0.11, –0.30, 0.26) formed by the phenyl rings of the Dppe ligands of six cluster cations. Weak hydrogen bonds Br(1)···C(4S)', 2.643 Å; Br(1)···C(2S), 2.759 Å; Br(1)···C(1S)', 3.025 Å are observed between the Br^-anion and CH_2Cl_2 molecules.

The temperature dependence of μ_{eff} of the crystalline phase of **III** · $4CH_2Cl_2$ is shown in Fig. 2. At 300 K, the value of μ_{eff} equals 3.76 μ_B and remains almost unchanged with the temperature decrease to 70 K. Below 70 K μ_{eff} somewhat decreases, reaching 2.97 μ_B at 5 K. The value of μ_{eff} in the temperature range from 70 to 300 K is consistent with a theoretical purely spin value of 3.87 μ_B for noninteracting paramagnetic centers with the spin $S = 3/2$ at $g = 2$. The magnetochemical data show that the scheme of molecular orbitals calculated for bromide cluster **I** can also be applied to **III** and, thus, three unpaired electrons lie on the doubly degenerate HOMO and nondegenerate HOMO-1 [4].

Thus, it was found that both the cluster core and its high-spin state were retained upon the replacement of the halide ions of the triangular rhenium cluster $[Re_3S_4(Dppe)_3Hal_3]Br$ (Hal = Br, Br/Cl) by thiocyanate anions.

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Table 2. Selected bond lengths (Å) in structure **III** · $4CH_2Cl_2$ and its analogs

Bond	**III** · $4CH_2Cl_2$	**I**	**II**	$[Mo_3S_4(Dppe)_3Br_{0.75}Cl_{2.25}]$ $(BF_4)_{0.5}Cl_{0.5}$ [9]
M–M	2.777(10)	2.780(9)	2.775(4)	2.777 [6]
M–(μ_3-S)	2.352(2)	2.344(4)	2.340(5)	2.359 [5]
M–(μ-S)	2.299(7)^a 2.328(7)^b	2.283(9)^a 2.327(5)^b	2.296(13)^a 2.336(10)^b	2.280 [5]^a 2.320 [4]^b
M–P	2.520(11)^c 2.511(1)^d	2.536(15)^c 2.511(8)^d	2.522(7)^c 2.504(7)^d	2.658 [12]^c 2.576 [6]^d
M–X	2.23(2)^e	2.586(12)^f	2.549(11)^g	2.51 [4]^g

^{a} *Trans*-(μ-S), ^{b} *trans*-X, ^{c} *trans*-(μ_3-S), ^{d} *trans*-(μ-S), ^{e} X = NCS, ^{f} X = Br, and ^{g} X = Br/Cl.

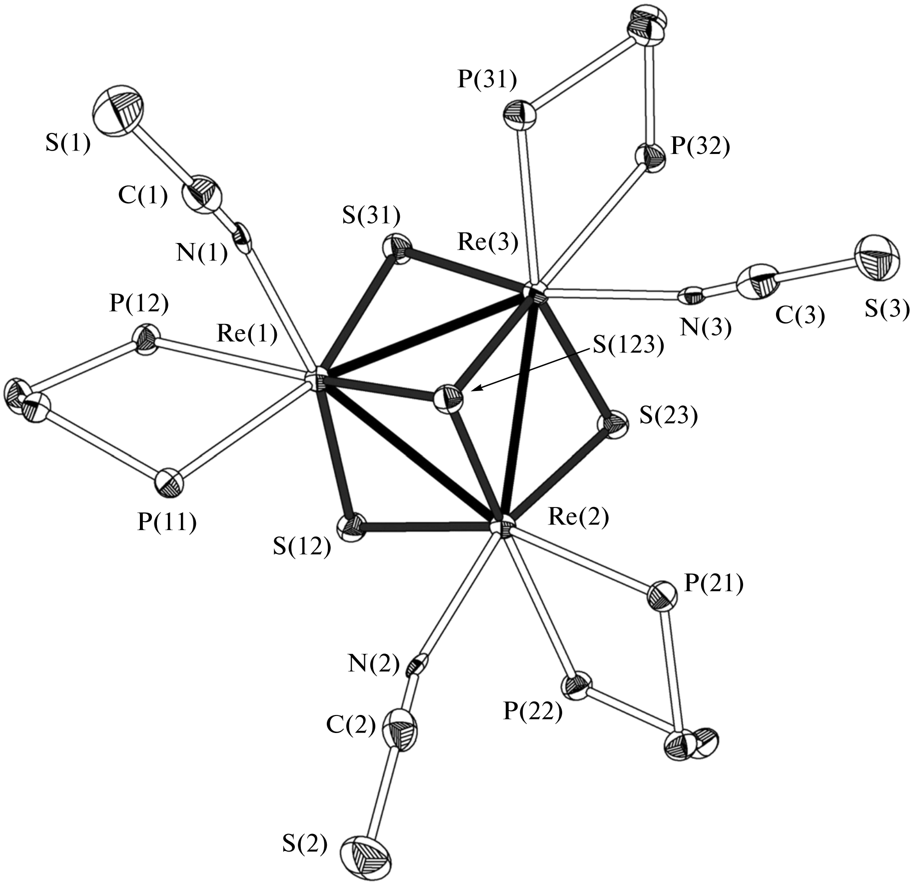

Fig. 1. Structure of cluster cation **III'**. Hydrogen atoms and phenyl rings of the Dppe ligands are omitted. Thermal ellipsoids of 50% probability are shown.

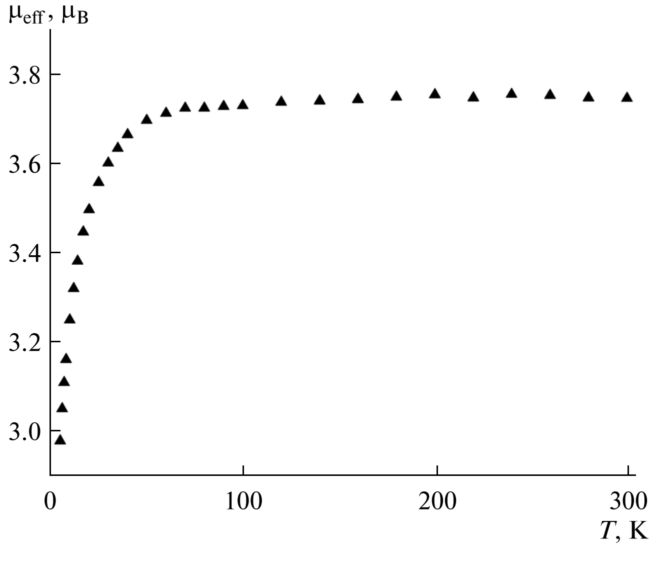

Fig. 2. Temperature dependence of the effective magnetic moment of the crystalline phase of **III** · $4CH_2Cl_2$.

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REFERENCES

1. Llusar, R., Uriel, S., Vicent, C., et al., *J. Am. Chem. Soc.*, 2004, vol. 126, p. 12071.
2. Feliz, M., Llusar, R., Uriel, S., et al., *Chem.-Eur. J.*, 2004, vol. 10, p. 4308.
3. Krackl, S., Alberola, A., Llusar, R., et al., *Inorg. Chim. Acta*, 2010, vol. 363, p. 4197.
4. Petrov, P.A., Virovets, A.V., Bogomyakov, A.S., et al., *Chem. Commun.*, 2012, vol. 48, p. 2713.
5. Fedin, V.P., Elsegood, M.R.J., Clegg, W., and Sykes, A.G., *Polyhedron*, 1996, vol. 15, p. 485.
6. Gordon, A. and Ford, R., *The Chemist's Companion: A Handbook of Practical Data, Techniques, and References*, New York: Wiley, 1972.
7. *APEX2 (Version 1.08), SAINT (Version 7.03), SADABS (Version 2.11) and SHELXTL (Version 6.12). Bruker Advanced X-ray Solutions*, Madison, (WI, USA), 2004.

8. Cotton, F.A. and Llusar, R., *Polyhedron*, 1987, vol. 6, p. 1741.
9. Estevan, F., Feliz, M., Llusar, R., et al., *Polyhedron*, 2001, vol. 20, p. 527.
10. Basallote, M.G., Estevan, F., Feliz, M., et al., *Dalton Trans.*, 2004, p. 530.
11. Adonin, S.A., Abramov, P.A., Virovets, A.V., et al., *Russ. J. Coord. Chem.*, 2010, vol. 36, no. 9, p. 637.
12. Mironov, Y.V., *Polyhedron*, 2000, vol. 19, p. 437.
13. Yoshimura, T., Chen, Z.-N., Itasaka, A., et al., *Inorg. Chem.*, 2003, vol. 42, p. 4857.
14. Shibahara, T., Yamasaki, M., Sakane, G., et al., *Inorg. Chem.*, 1992, vol. 31, p. 640.
15. Fedin, V.P., Sokolov, M.N., Virovets, A.V., et al., *Polyhedron*, 1992, vol. 11, p. 2973.
16. Sokolov, M.N., Dybtsev, D.N., Virovets, A.V., et al., *Inorg. Chem.*, 2002, vol. 41, p. 1136.
17. Sokolov, M., Esparza, P., Hernandez-Molina, R., et al., *Inorg. Chem.*, 2005, vol. 44, p. 1132.

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