Magnetic Anisotropy of New Layered Copper(II) Bromide Complexes of 1-Substituted Tetrazoles

Yurii Shvedenkov,*[a] Mark Bushuev,[a] Galina Romanenko,[b] Ludmila Lavrenova,[a] Vladimir Ikorskii,[b] Pavel Gaponik,[c] and Stanislav Larionov[a]

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Two new isostructural complexes, dibromobis(1-ethyltetrazole)copper(II) (**1**) and dibromobis(1-hexyltetrazole)copper(II) (**2**), have been synthesised. Each bromine atom in the crystal structure of **1** and **2** is bonded to two copper atoms to give rise to a polymeric corrugated network. The polymeric layers are distinctly separated by tetrazole ligands. Both solids exhibit a phase transition to the ferromagnetic state with Curie temperatures of 8.5 K and 8.9 K for **1** and **2**, respectively, and a strong anisotropy of the magnetic susceptibility below the ordering temperature. The easy magnetisation axis lies along the monoclinic axis, and the hard magnetisation axis is orthogonal to the polymeric layers. Effective anisotropy fields were estimated as (720–3020 Oe).

Introduction

In the design of new molecular magnets capable of magnetic phase ordering it is necessary to satisfy at least two conditions: the crystal structures of such compounds should be polymeric (2D or 3D), and the formed exchange channels should have sufficient efficiency for the magnetic ordering at experimentally observable temperatures.[1] One of the strategies to obtain such coordination compounds is to use ligands that are potentially capable of realizing a bridging function. Halogen atoms and polynitrogen heterocycles are particularly useful in this respect. It is known that the combination of Cu^{II} salts with heterocyclic azole ligands leads to the formation of mononuclear,[2–5] polynuclear[6–9] and even polymeric[10–15] complexes. For the majority of polymeric complexes one or more of the bridges are *N,N′*-didentate divided.[12,16,17] As a result the Cu–Cu distances in these cases are considerably increased. The formation of coordination compounds with a square polymeric lattice of copper atoms and halide ions only is an occasional and specific case for complexes with polynitrogen heterocycle ligands.[18–25] Note that even the use of 1-substituted tetrazoles with furcated substitutes or disubstituted tetrazoles leads to the formation of chain or mononuclear complexes.[10,13,14] From this point of view, 1-substituted tetrazole derivatives with non-furcated substitutes are unique ligands for the design of molecular magnets with a two-dimensional crystal structure.

We have previously reported the formation of layered polymeric structures for a whole series of complexes of Cu^{II} and Co^{II} chlorides with 1-substituted tetrazoles (Rtz, R = ethyl, allyl, vinyl) with the general stoichiometry $[M(Rtz)_2Cl_2]$ (M = Cu^{II}, Co^{II}).[18–23,26] The $[Cu(Rtz)_2Cl_2]$ complexes undergo a ferromagnetic transition at temperatures lower than 10 K and $[Co(alltz)_2Cl_2]$[26] undergoes a phase transition to an antiferromagnetic state with a weak ferromagnetic behaviour at 99.6 K. Recently, complexes $[Cu(teec)_2A_2]$ [teec = 1-(2-chloroethyl)tetrazole; A = Cl^-, Br^-, NO_3^-] have been prepared and studied in detail.[4,25] It was found that $[Cu(teec)_2Cl_2]$ and $[Cu(teec)_2Br_2]$ are soft ferromagnets with T_c = 4.75 K and 8.01 K, respectively.[25] On the other hand, active studies of molecular magnets have stimulated the investigation of the anisotropy of magnetic properties with single crystalline samples. The first study of the magnetic anisotropy of a layered polymeric complex containing a tetrazole derivative was done with $[Co(alltz)_2Cl_2]$.[27]

This work continues our systematic investigation of the synthesis and characterisation of Cu^{II} halide complexes with tetrazoles. We report the preparation, structure and studies of the anisotropy of magnetic properties of a new layered polymer of Cu^{II} bromide with 1-ethyl- and 1-hexyltetrazoles.

Results and Discussion

Single crystals of complexes dibromobis(1-ethyltetrazole)copper(II) (**1**) and dibromobis(1-hexyltetrazole)copper(II) (**2**)

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[a] Nikolaev Institute of Inorganic Chemistry SB RAS,
Lavrent'ev Ave., 3, Novosibirsk, 630090, Russia
Fax: +7-3832-33-1399
E-mail: schved@tomo.nsc.ru
[b] International Tomography Center SB RAS,
Institutskaya Str., 3a, Novosibirsk, 630090, Russia
Fax: +7-3832-33-1399
E-mail: romanenk@tomo.nsc.ru
[c] Instituite of Physico-Chemical Problems, Belarussian State University,
Leningradskaya Str., 14, Minsk, 220050, Belarus
Fax: +7-3832-33-1399
E-mail: gaponik@bsu.by

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for both a crystal structure determination and an investigation of the magnetic properties were grown from EtOH solutions under ambient conditions. Note that crystals obtained in a thermostat, while having a nice appearance, appeared to be twins or joints. This may be caused by vibrations originating from the thermostat′s operation.

The values of bond lengths and angles of the complexes are listed in Table 1.

In these complexes the copper atom coordinates two tetrazole molecules in the equatorial plane (*trans* to each other) and two bromine atoms to form $[Cu(Rtz)_2Br_2]$ complex fragments (Figure 1).

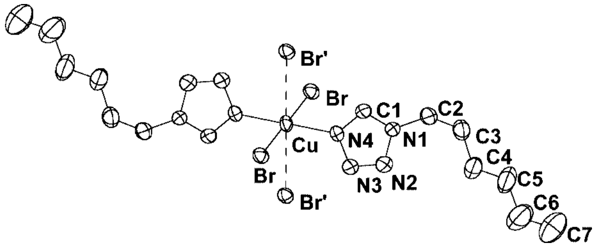

Figure 1. $[Cu(Rtz)_2Br_2]$ molecular structure exemplified by **2**. Hydrogen atoms have been omitted for clarity.

The structures of both complexes are very similar. The environment of the copper atom is a centrosymmetric square bipyramid due to additional bonds to the bromine atoms of neighbouring $\{Cu(Rtz)_2Br_2\}$ fragments. Thus, the bromine atoms form non-symmetric bridges (the Cu–Br–Cu angles are equal to 138.55° and 138.16° for **1** and **2**, respectively) and connect $\{Cu(Rtz)_2Br_2\}$ fragments into layers (Figure 2) parallel to the (100) plane. The tetrazole molecules separate the layers from each other. The tetrazole fragments are practically planar reflecting the π-conjugation in the heterocycle. A comparison of the bond lengths in the tetrazole ring allows us to distinguish between "single" and "double" bonds [N(1)–N(2), N(3)–N(4) and N(2)=N(3)]. The "double" C(1)=N(4) and "single" C(1)–N(1) bond lengths are practically identical in both compounds. The plane of the tetrazole fragment in both complexes does not coincide with the equatorial plane of the tetragonal bipyramid of the copper atom and makes angles of 55.8(1)° and 57.7° for **1** and **2**, respectively.

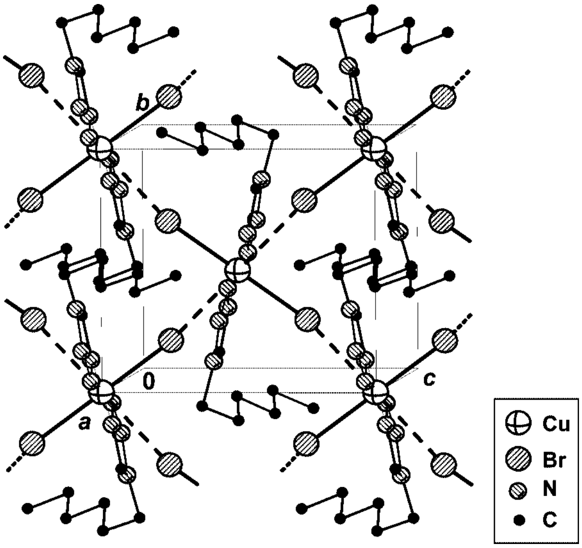

Figure 2. Fragment of $[Cu(Rtz)_2Br_2]$ polymeric layer structure exemplified by **2**. Hydrogen atoms have been omitted for clarity.

The N(1)–C(2) distance is typical for a single bond. The interlayer distance in **2** (19.750 Å) is much greater than in **1** (12.328 Å) because the alkyl groups protrude into the interlayer space. The distances between adjacent Br atoms are close to double the van der Waals radius [Br···Br′ = 3.8702(6) Å in **1** and 3.883(5) Å in **2**].

A comparison of the geometrical characteristics in **1**, **2** and previously reported $[Cu(Rtz)_2Cl_2]$ complexes[21,22,24,26] shows that the Cu–N(4) distances are practically identical for all compounds and are in the range of 1.98–1.99 Å. The lengths of the Cu–Br bonds in the equatorial plane are 2.43–2.45 Å, whereas the lengths of the axial Cu–Br′ bonds are equal to 3.08–3.09 Å. The axial Cu–Cl distances, as a rule, are also approximately 3 Å, and differ from the axial Cu–Br lengths only slightly. The Cu–A–Cu angles, where A = Cl^-, Br^-, are essentially independent of A (136–139°).

The dependencies $\mu_{\text{eff}}(T)$ and $1/\chi(T)$ above 10 K, as measured on polycrystalline samples, are presented in Figure 3 and Figure 4. At room temperature, μ_{eff} of complexes **1**, **2** are 1.869 μ_B and 1.884 μ_B, respectively, which correspond to the

Table 1. Relevant bond lengths [Å] and angles [°] in compounds **1** and **2**.

	1	**2**		**1**	**2**
Cu–N(4)	1.990(3)	1.982(3)	Cu–Br–Cu′	138.55(1)	138.16(1)
Cu–Br	2.4302(4)	2.4389(4)	N(4)–Cu–Br	90.12(9)	89.63(8)
Cu–Br′	3.0842(5)	3.0953(4)	N(4)–C(1)–N(1)	109.5(4)	109.0(4)
N(4)–C(1)	1.290(6)	1.304(5)	N(3)–N(4)–C(1)	106.8(4)	106.7(3)
N(3)–N(4)	1.346(5)	1.344(4)	N(3)–N(2)–N(1)	107.0(4)	107.2(3)
N(2)–N(3)	1.285(5)	1.289(4)	N(2)–N(3)–N(4)	109.1(4)	109.4(3)
N(1)–N(2)	1.346(5)	1.343(4)	C(1)–N(1)–N(2)	107.6(4)	107.7(3)
N(1)–C(1)	1.307(6)	1.315(5)	C(1)–N(1)–C(2)	130.5(4)	129.7(4)
N(1)–C(2)	1.472(6)	1.467(5)	N(2)–N(1)–C(2)	122.1(4)	122.6(3)
C(2)–C(3)	1.381(11)	1.487(7)	N(1)–C(2)–C(3)	113.6(7)	113.8(4)
C(3)–C(4)		1.504(7)	C(2)–C(3)–C(4)		116.8(4)
C(4)–C(5)		1.512(8)	C(3)–C(4)–C(5)		113.4(5)
C(5)–C(6)		1.488(10)	C(4)–C(5)–C(6)		114.1(6)
C(6)–C(7)		1.520(14)	C(5)–C(6)–C(7)		110.9(10)

magnetic moment for $S = 1/2$ with Cu^{II} g-factors equal to 2.158 and 2.175, respectively. At lower temperatures, μ_{eff} increases for compounds **1** and **2** (Figure 3), indicating that ferromagnetic exchange interactions dominate.

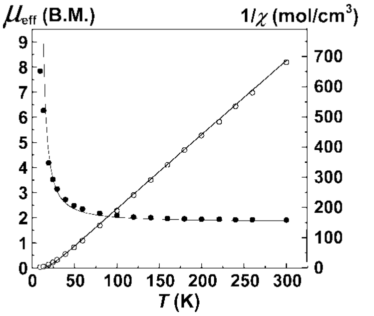

Figure 3. Dependencies $\mu_{eff}(T)$ (●) and $1/\chi(T)$ (○) in the paramagnetic region for **1**. Solid lines are the theoretical approximation.

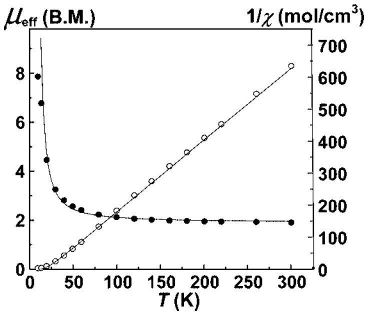

Figure 4. Dependencies $\mu_{eff}(T)$ (●) and $1/\chi(T)$ (○) in the paramagnetic region for **2**. Solid lines are the theoretical approximation.

The magnetic susceptibility follows the Curie–Weiss law [$\chi = C/(T - \theta)$] with the parameters given in Table 2. The values for the exchange parameter (J) between the Cu^{II} ions can be estimated from high-temperature data by series expansion for a two-dimensional Heisenberg model.[28]

Table 2. Magnetochemical parameters of **1** and **2**.

	C [cm^3 mol^{-1} K^{-1}]	θ [K]	J [K]	T_c [K]	H_x [Oe]	H_z [Oe]
1	0.414	19.9	8.77	8.5(3)	2550	720
2	0.409	24.2	9.11	8.9(5)	3020	860

For the high-temperature series expansion the J value is obtained by approximating the experimental dependencies from a known expression for the magnetic susceptibility: $\chi = Ng\beta^2 S(S+1)/3kT(1 + \sum_{n=1}^{10} a_n K^n)$, where $K = 2J/kT$ and a_n is a coefficient for a square-planar lattice. We applied the above formula to the description of $\mu_{eff}(T)$ dependencies of complexes in the temperature interval 10–300 K. The optimal J parameters (Table 2) were calculated this way. The relevant theoretical curves are presented in Figure 3 and 4 as solid lines.

Below 10 K the magnetic properties of **1** and **2** were investigated with single crystalline samples. Figure 5 and Figure 6 show the temperature dependence of the susceptibilities measured in a small magnetic field (1.2 ± 0.5 Oe) and the main curves of magnetisation $\sigma(H)$ at 4.5 K.

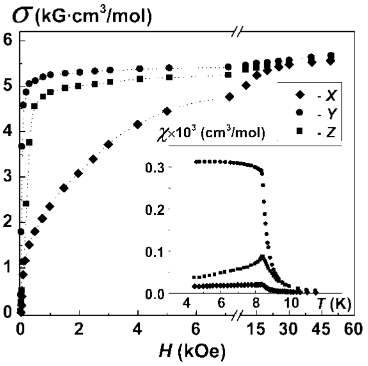

Figure 5. Magnetisation curves (4.5 K) and low field $\chi(T)$ curves in the transition area (insert) for single crystalline **1**.

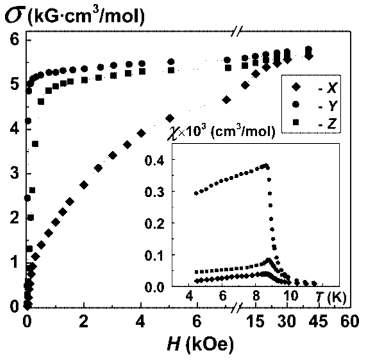

Figure 6. Magnetisation curves (4.5 K) and low field $\chi(T)$ curves in the transition area (insert) for single crystalline **2**.

Both solids exhibit a phase transition to the ferromagnetic state with $T_c = 8.5$ K and 8.9 K for **1** and **2**, respectively, and a strong anisotropy of the magnetic susceptibility below the ordering temperature (Figure 5 and 6).

By using the known expression $T_c = 4\pi J/\ln(J/J')$[29] (J' is the interlayer interaction) for layered Heisenberg magnets it is possible to estimate the ratio J'/J. For both compounds the ratio J'/J is close to 3×10^{-6} K, which is in good agreement with results for similar systems.

The maximal value of σ at $T = 4.5$ K is more than 5700 G cm^3 mol^{-1}, which is close to the saturation magnetisation ($Ng\beta S = 5585$ G cm^3 mol^{-1}) for ferromagnetically coupled spins ($S = 1/2$) with $g = 2$. No hysteresis effects were detected for single crystals of **1** and **2** subjected to supermagnetisation. This fact indicates that complexes **1** and **2** behave as soft ferromagnets. The $\chi(T)$ and $\sigma(H)$ curves measured along different directions show essential anisotropy. In both cases, the easy magnetisation axis lies along the y axis, which is the only symmetry axis of the crystals. The hard magnetisation axis coincides with the X direction, which is orthogonal to the polymeric layers. The anisotropy of the magnetic properties in the plane of the polymeric layers (YZ) is much less than in the perpendicular direction as a consequence of the quasi-two-dimensional magnetic nature of the investigated compounds. Thus, the observed anisotropy in **1** and **2** should be of the “easy plane” type. Anisotropic energies were estimated for the single crystals of **1** and **2**. The free energy of magnetic anisotropy may be represented as $F_i \approx -H_i\sigma_{\text{sat}}$, where $i = X, Z$, H_i is the effective anisotropy field and σ_{sat} is the saturation magnetisation.[30] The energy F_i was determined from the experimental magnetisation curves by numerical integration: $F_i = \int_0^{H_{\max}} \sigma_Y(H)dH - \int_0^{H_{\max}} \sigma_i(H)dH$, where $H_{\max}$ is the maximum field during the measurements. The calculated effective anisotropy fields for the complexes are presented in Table 2. It is noteworthy that the calculated anisotropy fields of **1** and **2** are approximately three times larger than in layered polymeric CuL_2 complexes of 3-imidazoline nitroxides.[31] This is probably due to the fact that the organic radical is an isotropic paramagnetic centre, therefore in complexes CuL_2 the “effective concentration” of anisotropic magnetic centres is three times lower than in **1** and **2**. On the other hand, the estimated anisotropy fields of the ferrimagnetic compound [Mn(hfac)$_2$(NIT-*i*Pr)] (NIT-*i*Pr = derivative of 2-imidazoline nitroxide) are H_x = 1200 Oe and H_z = 7500 Oe.[32] Such large anisotropy fields for a complex of such a weakly anisotropic ion as Mn^{II} are probably caused by the low-dimensional polymeric chain structure of this compound. Thus, the anisotropy of solids increases not only for complexes with more anisotropic metal ions, but also for solids with lower dimensionality of the crystal structure. For coordination compounds the energy of the anisotropy combined with dipolar interactions contributes greatly to the value of the ordering temperature.[33] From this point of view the increase of anisotropy of a magnetic system can be considered as one of the ways to increase the transition temperature.

Conclusions

The magnetic properties of single crystalline samples of Cu^{II} bromide complexes of 1-substituted tetrazoles have been investigated. In the layered polymer complexes **1** and **2**, we have found a phase transition to the ferromagnetic state at T_c = 8.5 K (**1**) and 8.9 K (**2**) and a strong anisotropy of the magnetic susceptibility below the magnetic ordering temperature.

Experimental Section

General Remarks: All commercially available reagents were used as purchased. 1-Ethyltetrazole (ettz) and 1-hexyltetrazole (htz) were prepared by literature methods.[34] The copper content was determined by complexometric titration, with the samples being mineralized in a 1:1 mixture of concentrated H_2SO_4 and $HClO_4$. Elemental analysis was performed with a Carlo–Erba analyzer.

Dibromobis(1-ethyltetrazole)copper(II) (1) and Dibromobis(1-hexyltetrazole)copper(II) (2): A solution of ettz (0.40 g, 4 mmol) or htz (0.62 g, 4 mmol) in 16 mL of a 1:1 ethanol/hexane mixture was added to a solution of $CuBr_2$ (0.45 g, 2 mol) in 10 mL the same mixture. A brown precipitate formed, which was filtered off, washed with ethanol and dried in air. Yield of **1**: 0.84 g (80%); **2**: 0.62 g (75%).
1: $C_6H_{12}Br_2CuN_8$ (419.56): calcd. C 17.2, H 2.9, Cu 15.1, N 26.7; found C 16.7, H 2.9, Cu 15.4, N 27.1.
2: $C_{14}H_{28}N_8Br_2Cu$ (531.78): calcd. C 31.6, H 5.3, Cu 11.9, N 21.1; found C 31.5, H 5.2, N 20.3, Cu 12.1.
For growing large single crystals the initial solids were dissolved in EtOH at 43 °C. Then, as much solvent as possible was removed with a stream of air with the condition that crystallisation did not occur at room temperature. After that the flasks were stoppered and allowed to stand at ambient temperature. Dark-brown, parallelepiped-shaped single crystals of **1** and **2** with a maximal appearance of up to 3 × 3 × 0.1 mm grew after approximately one month.

X-ray Crystallographic Study: Single crystal data for **1** and **2** were collected on a SMART APEX Bruker AXS automatic diffractometer at ambient temperature using the standard procedure (Mo-K_α radiation). The structures were solved by direct methods. The full-matrix least-squares refinement was performed anisotropically for non-hydrogen atoms and isotropically for hydrogens. Some H-atoms were localised in difference electron density syntheses; the others were generated theoretically. All structure solution and refinement calculations were carried out with SHELXTL software.[35] The crystal data for the compounds and details of experiment, as well as selected bond lengths and angles are given in Table 1 and Table 3.

Table 3. Crystal data and experimental details.

	1	2
Formula	$C_6H_{14}Br_2CuN_8$	$C_{14}H_{28}Br_2CuN_8$
T [K]	295	295
Space group	$P2_1/c$	$P2_1/c$
Z	2	2
a [Å]	12.655(2)	20.076(3)
b [Å]	6.915(1)	6.9430(9)
c [Å]	7.668(1)	7.675(1)
β [°]	103.053(2)	100.344(2)
V [Å^3]	653.7(2)	1052.4(2)
D_c [g cm^{-3}]	2.142	1.678
μ [mm^{-1}]	7.776	4.849
I_{hkl} meas./unique	2352/940	4330/1516
R_{int}	0.0218	0.0896
I_{hkl}/N	940/95	1516/172
Goof	0.998	0.845
R_1 [$I > 2\sigma(I)$]	0.0278	0.0338
wR_2	0.0707	0.0750
R_1	0.0309	0.0384
wR_2	0.0726	0.0777

Magnetic Measurements: The magnetochemical experiments were performed with an MPMS-5S (“Quantum Design”) SQUID magnetometer at temperatures from 4.5 K to 300 K in a homogeneous external magnetic field of up to 49.5 kOe. Magnetic measurements on single crystals were performed in three mutually orthogonal directions (X, Y, Z). The Y and Z directions were aligned with the crystallographic b and c axes. The molar magnetic susceptibility, χ, of the complexes was calculated by using Pascal’s additive scheme including diamagnetic corrections and taking into account the temperature-independent paramagnetism of Cu^{II} ions, which was taken to be 60×10^{-6} cm^3 mol^{-1}. In the paramagnetic region the effective magnetic moment was calculated with the formula $\mu_{\text{eff}} = [(3k/N_A\beta^2)\chi T]^{1/2} \approx (8\chi T)^{1/2}$, where k is Boltzmann’s constant, N_A is the Avogadro number and β is the Bohr magneton. The magnetic phase transition temperature was determined as the extremum of the derivative of the magnetic susceptibility with respect to temperature $\partial\chi/\partial T$. The magnetisation dependencies $\sigma(H)$ of the single crystals below the transition temperature were taken into account for the demagnetisation field of the sample. The real field in the crystal was calculated for each direction by the formula $H_i = H - N_i\sigma_i$, where $i = X, Y, Z$; N is the demagnetisation factor evaluated using the tables for the disk sample.[36]

CCDC-241146 (for **1**) and -241147 (for **2**) contain the supplementary crystallographic data for this paper data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] V. I. Ovcharenko, R. Z. Sagdeev, *Russ. Chem. Rev. Int. Ed. Engl.* **1999**, *68*, 345–363.
[2] P. E. M. Wijnands, J. S. Wood, J. Reedijk, W. J. A. Maaskant, *Inorg. Chem.* **1996**, *35*, 1214–1222.
[3] J. G. Haasnoot, *Coord. Chem. Rev.* **2000**, *200*, 131–185.
[4] A. F. Stassen, W. L. Drissen, J. P. Haasnoot, J. Reedijk, *Inorg. Chim. Acta* **2003**, *350*, 57–61.
[5] A. S. Lyakhov, P. N. Gaponik, S. V. Voitekhovich, D. O. Ivashkevich, P. S. Putleva, L. S. Ivashkevich, *Acta Crystallogr., Sect. C* **2001**, *57*, 1374–1376.
[6] W. Clegg, J. R. Nicholson, D. Collison, C. D. Garner, *Acta Crystallogr., Sect. C* **1988**, *44*, 453–461.
[7] F. S. Keij, J. G. Haasnoot, A. J. Oosterling, J. Reedijk, *Inorg. Chim. Acta* **1991**, *181*, 185–193.
[8] C. J. Campbell, W. L. Driessen, J. Reedijk, W. J. Smeets, A. L. Spek, *J. Chem. Soc., Dalton Trans.* **1998**, 2703–2706.
[9] A. V. Virovets, G. A. Bikzhanova, L. G. Lavrenova, *Russ. J. Struct. Chem. Int. Ed. Engl.* **2001**, *42*, 989–994.
[10] A. S. Lyakhov, P. N. Gaponik, M. M. Degtyarik, V. E. Matulis, L. S. Ivashkevich, *Acta Crystallogr., Sect. C* **2003**, *59*, m90–m92.
[11] Y. Garcia, P. J. van Koningsbruggen, G. Bravic, P. Guionneau, A. Chasseau, G. L. Cascarano, J. Moscovici, K. Lambert, A. Michalowicz, O. Kahn, *Inorg. Chem.* **1997**, *36*, 6357–6365.
[12] M. Lagrenee, S. Sueur, J. P. Wignacourt, B. Mernari, A. Boukhari, *J. Chim. Phys. Phys.-Chim. Biol.* **1991**, *88*, 2075–2089.
[13] D. O. Ivashkevich, M. M. Degtyarik, P. N. Gaponik, A. S. Lyakhov, *Acta Crystallogr., Sect. C* **2002**, *58*, m288–m301.
[14] D. O. Ivashkevich, A. S. Lyakhov, M. M. Degtyarik, P. N. Gaponik, *Acta Crystallogr., Sect. E* **2003**, *E59*, m14–m16.
[15] A. V. Virovets, G. A. Bikzhanova, N. V. Podberezskaya, L. G. Lavrenova, *Russ. J. Struct. Chem. Int. Ed. Engl.* **1997**, *38*, 103–109.
[16] S. Decurtins, H. W. Schmalle, P. Schneuwly, L. M. Zheng, J. Ensling, A. Hauser, *Inorg. Chem.* **1995**, *35*, 5501–5506.
[17] G. A. van Albada, R. C. Guijt, J. G. Haasnoot, M. Lutz, A. L. Spek, J. Reedijk, *Eur. J. Inorg. Chem.* **2000**, 121–126.
[18] L. G. Lavrenova, A. N. Bogatikov, L. A. Sheludyakova, V. N. Ikorskii, S. V. Larionov, P. N. Gaponik, *J. Inorg. Chem. USSR Int. Ed. Engl.* **1991**, *36*, 693–698.
[19] L. G. Lavrenova, V. N. Ikorskii, S. V. Larionov, A. N. Bogatikov, P. N. Gaponik, *J. Inorg. Chem. USSR Int. Ed. Engl.* **1993**, *38*, 1416–1417.
[20] A. V. Virovets, I. A. Baydina, V. I. Alekseev, N. V. Podberezskaya, L. G. Lavrenova, *Russ. J. Struct. Chem. Int. Ed. Engl.* **1996**, *37*, 288–294.
[21] A. V. Virovets, N. V. Podberezskaya, L. G. Lavrenova, G. A. Bikzhanova, *Acta Crystallogr., Sect. C* **1995**, *51*, 1084–1087.
[22] L. G. Lavrenova, A. N. Bogatikov, V. N. Ikorskii, L. A. Sheludyakova, E. G. Boguslavskii, P. N. Gaponik, S. V. Larionov, *Russ. J. Inorg. Chem. Int. Ed. Engl.* **1996**, *41*, 406–409.
[23] L. G. Lavrenova, G. A. Bikzhanova, A. N. Bogatikov, V. N. Ikorskii, L. A. Sheludyakova, A. V. Virovets, N. V. Podberezskaya, P. N. Gaponik, S. V. Larionov, *Russ. J. Inorg. Chem. Int. Ed. Engl.* **1996**, *41*, 587–592.
[24] D. O. Ivashkevich, A. S. Lyakhov, P. N. Gaponik, A. N. Bogatikov, A. A. Govorova, *Acta Crystallogr., Sect. C* **2001**, *C57*, m335–m337.
[25] A. F. Stassen, H. Kooijman, A. L. Spec, L. Jos de Jongh, J. P. Haasnoot, J. Reedijik, *Inorg. Chem.* **2002**, *41*, 6468–6473.
[26] Yu. G. Shvedenkov, A. V. Virovets, L. G. Lavrenova, *Russ. Chem. Bull. Int. Ed. Engl.* **2003**, *52*, 1353–1357.
[27] Yu. G. Shvedenkov, V. N. Ikorskii, L. G. Lavrenova, *J. Phys. IV France* **2004**, *114*, 649–650.
[28] R. Navarro, in *Magnetic Properties of Layered Transition Metal Compounds* (Ed.: L. J. De Jongh), Kluwer Academic Publishers, The Netherlands, **1990**, 105–190.
[29] V. L. Pokrovsky, G. V. Uimin, in *Magnetic Properties of Layered Transition Metal Compounds* (Ed.: L. J. De Jongh), Kluwer Academic Publishers, The Netherlands, **1990**, 53–102.
[30] S. V. Vonsovskii, *Magnetism*, Izdatelstvo "Nauka", Moscow, **1971**, p. 476.
[31] Y. Shvedenkov, V. Ikorskii, D. Guschin, E. Fursova, V. Ovcharenko, *Polyhedron* **2001**, *20*, 1207–1213.
[32] A. Caneschi, D. Gatteschi, J.-P. Renard, P. Rey, R. Sessoli, *Inorg. Chem.* **1989**, *28*, 1976–1980.
[33] E. V. Kuzmin, G. A. Petrakovsky, *Izvestiya Vuzov MV I SSO SSSR Fizika* **1988**, *3*, 94–101.
[34] P. N. Gaponik, V. P. Karavai, Yu. V. Grigor'ev, *Chem. Heterocycl. Compd. Int. Ed. Engl.* **1985**, *21*, no. 11, 1255–1258.
[35] *SHELXTL*, version 6.14, Bruker AXS, 8/06/00.
[36] V. I. Chechernikov, *Magnitnie izmereniya* (Ed.: E. I. Kondorskii), Izdatelstvo Moskovskogo Universiteta, **1963**, p. 57.

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