New Layered Polymeric Metamagnet Based on Copper(II) Complex with 3-Imidazoline Nitroxide

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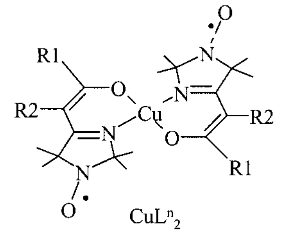
A new complex, bis[4-(2-oxido-1-butenyl)-2,2,5,5-tetramethylimidazolidine-1-oxyl]copper(II) (CuL^{Et}_2), has been synthesized. The synthesis, characterization, and magnetic properties as well as the crystal structure of CuL^{Et}_2 have been studied. The layered solid of the complex possesses a metamagnetic phase transition at 4.5 K and shows strong anisotropy of magnetic properties below the ordering temperature. The easy magnetization axis lies along the *b* axis. The hard magnetization axis is orthogonal to the polymeric layers. Effective anisotropy fields have been estimated ($H_\perp$ = 1390 Oe, $H_\parallel$ = 420 Oe).

Introduction

The design of molecular magnets demands the ability to engineer the desired crystal structure and the means to control the efficiency of interactions of a diverse nature between the paramagnetic centers.[1] One of the peculiarities of molecular magnets derived from coordination compounds is considerable local and bulk anisotropy introduced by transition-metal ions. The majority of coordination compounds have low symmetry in the solid phase and their crystal structures have low dimensionality. The energy of anisotropy of such systems depends appreciably on the dimensionality of the crystal structure and on the contribution of dipolar interactions to the onset of magnetic ordering.[2] The importance of the dimensionality is well illustrated by comparison of the chain polymeric (1D) complex $Mn(hfac)_2$NIT-*i*Pr (NIT-*i*Pr = derivative of 2-imidazoline nitroxide)[3] and of layered polymeric (2D) complex CuL_2 (L = derivatives of 3-imidazoline nitroxide),[4] the effective anisotropy field being approximately five times larger for the former. Also, anisotropic interactions of a nonexchange nature lead to the appearance of metamagnetism in coordination compounds such as $[(CH)_3NH]CuCl_3{\cdot}2H_2O$[5] and CuL^{Me}_2.[4]

With this contribution we continue our systematic studies on the magnetic anisotropy of heterospin compounds based on Cu^{II} complexes with enaminoketone derivatives of 3-imidazoline nitroxide.

These compounds provide a unique series of solids possessing similar layered topology but different structural details, thus providing a very good basis for revealing the correlations between structure and magnetic anisotropy. In this work we report the results of the structural and magnetic investigation of the complex CuL^{Et}_2.



CuL^n_2

L	R1	R2
L^{Et}	Et	NC
L^{Me}	Me	NC
$L^{C(O)OEt}$	C(O)OEt	H
$L^{C(O)OMe}$	C(O)OMe	H

Results and Discussion

The compound under investigation is built from CuL^{Et}_2 molecules, the copper atom occupying the inversion center [1/2,0,1/2]. The closest coordination environment of copper is formed by two nitrogens N(1) and two oxygens O(1) belonging to the enaminoketone moieties (Figure 1).

The bond lengths and angles within the molecules have the usual values. The axial positions around the copper atom are occupied by two nitroxide oxygens O(2) at a distance of 2.584(3) Å. The Cu–O(2) bond is almost perfectly perpendicular to the coordination square, the deviation being only 0.3°. With a connectivity of four at the copper atom, the molecules arrange into the 4^4 (in Wells notation[6]) chicken-wire nets parallel to the (0,0,1) plane (Figure 2). Within the frame of the *Pbca* space group the neighboring polymeric nets are related with the *c* glide plane with a net-to-net separation of 11.978 Å, as measured between the closest copper atoms. This is somewhat longer than the equivalent separation in CuL^{Me}_2, which is equal to 11.869 Å. This difference in separation between iso-

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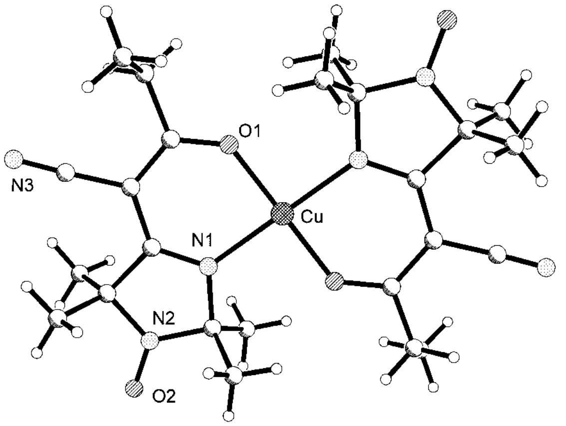

Figure 1. The molecule CuL^{Et}_2.

structural CuL^{Me}_2 and CuL^{Et}_2 is due to the different sizes of the Me and Et substituents which propagate into the interlayer space.

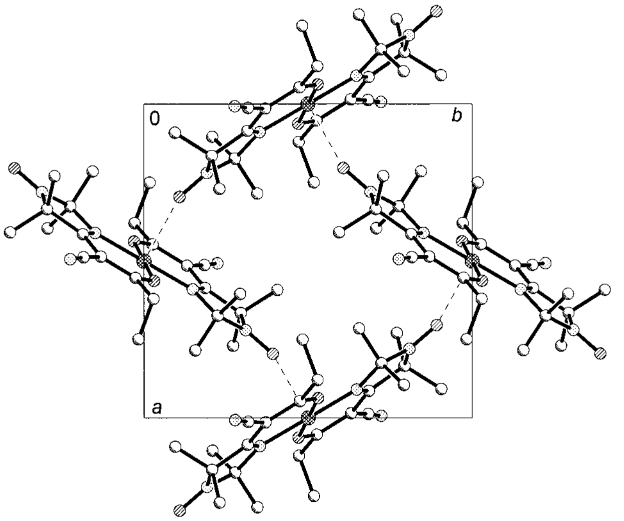

Figure 2. Fragment of the polymeric layered structure of CuL^{Et}_2 projected onto the (001) plane. Hydrogen atoms are omitted for clarity.

Figure 3 illustrates the effective magnetic moment of CuL^{Et}_2 measured along different crystallographic directions above 14 K. In this temperature range, CuL^{Et}_2 behaves as a paramagnet with dominating ferromagnetic exchange interactions between paramagnetic centers. The CuL^{Et}_2 complex possesses two main exchange channels. The first exchange channel is the intramolecular indirect exchange between the nitroxide and copper spins through the heterocycle of the ligand. The other exchange pathway is the direct exchange between the copper(II) ion and the nitroxide group belonging to the adjacent $\{CuL_2\}$ bis-chelate fragment. Both exchange pathways propagate ferromagnetic interactions[7] resulting in the rise of the $\mu_{eff}(T)$ curves with decreasing temperature. The $\mu_{eff}(T)$ curves measured along different directions are quite close (Figure 3). The observed discrepancy in the paramagnetic region is caused by the anisotropy of the copper(II) g-factors. An approximation of the experimental data in the 100–300 K temperature interval by the Curie–Weiss equation results in the optimal parameters $C_a = 1.22$, $C_b = 1.24$, $C_c = 1.15\,cm^3\,K\,mol^{-1}$, and $\theta_a = 12.6$, $\theta_b = 13.8$, $\theta_c = 11.9$ K.

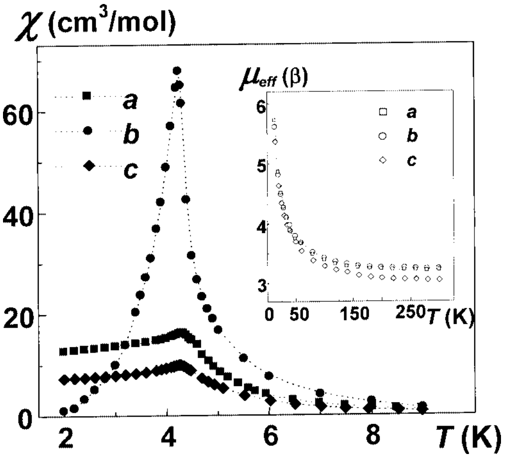

Figure 3. Low field $\chi(T)$ curves in the transition area and $\mu_{eff}(T)$ curves (inset) in the paramagnetic region for a CuL^{Et}_2 single crystal.

The set of constants obtained corresponds to **g**-tensor components along the directions of measurement: $g_a = 2.24$, $g_b = 2.29$, $g_c = 2.06$, which are in good agreement with g-factor values known for copper(II) coordination compounds.[8,9] The similarity of the Curie–Weiss parameters suggests that the CuL^{Et}_2 can be considered as an isotropic two-dimensional magnet.[10] On temperature lowering to 10 K, the CuL^{Et}_2 single crystal undergoes a phase transition to the magnetically ordered state. Measurements performed in zero magnetic field (1.2 ± 0.5 Oe) indicate that ordering occurs sharply at 4.5 K. Figure 4 shows the main curves of magnetization, $\sigma(H)$, at 2 K for the single crystal.

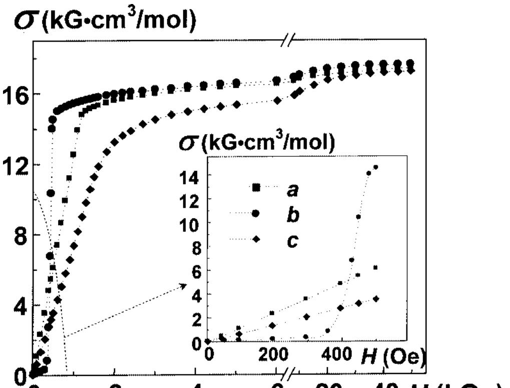

Figure 4. Magnetization curves for a CuL^{Et}_2 single crystal.

Below 400 Oe the magnetization of the CuL^{Et}_2 single crystal measured along unit-cell axes satisfies the equation $\sigma_i(H) = \chi_i H$, where $i = a, b, c$. Thus, a compensated antiferromagnetic structure is formed. At 2 K, the susceptibilities along a, b, and c are 12.515, 0.975, and 7.332 $cm^3\,mol^{-1}$), respectively. The susceptibility ratio along different directions unambiguously suggests that $\chi_{||}$ corresponds to the b axis, and $\chi_{\perp}$ to the a and c axes. As follows from the magnetization curves, at low fields the antiferromagnetic axis is *b* and the easy magnetization axis is *a*. As the crystal structure of CuL^{Et}_2 is layered polymeric with ferromagnetic exchange interactions dominating inside the layers, it is logical to assume that the antiferromagnetic structure is formed by the magnetic moments of ferromagnetically ordered layers. The interactions leading to the collinear antiferromagnetic structure forming in CuL^{Et}_2 probably have a dipolar nature. For $H > 400$ Oe, the $\sigma(H)$ curves become nonlinear. Magnetization along the *b* axis increases sharply and tends to saturation $Ng\beta S$ for an $S = 3/2$ system. This effect indicates a metamagnetic phase transition in CuL^{Et}_2 with the critical field $H_c = 440$ Oe. The given value of the critical field corresponds to the absolute magnitude of the energy of the interlayer interactions ($3\beta H$) equal to 0.088 K. At high magnetic fields, the $\sigma(H)$ curves measured along different directions diverge because of the *g*-factor anisotropy of the copper(II) ion (Figure 4). No hysteresis effects were detected when CuL^{Et}_2 was subjected to supermagnetization. Thus, the easy magnetization axis coincides with the crystallographic *b* axis. The hard magnetization axis is orthogonal to the polymeric layers. The transition found in CuL^{Et}_2 is characterized by a low critical field, which has the same order of magnitude as that found in coordination compounds $\{[(CH)_3NH]CuCl_3{\cdot}2H_2O$[5], CuL^{Me}_2[4]$\}$. This field is 10–30 kOe for classical metamagnets ($MnBr_2$, $FeCl_2$, $CoCl_2$). The anisotropy energies were estimated for the CuL^{Et}_2 single crystal. The free energy of magnetic anisotropy may be represented as $F_i \approx -H_i\sigma_{sat}$, where $i = a, c$; H_i is the effective anisotropy field, and σ_{sat} is saturation magnetization.[11] The energy F_i was determined from the experimental magnetization curves by the numerical integration:

$$F_i = \int_0^{H_{max}} \sigma_b(H)dH - \int_0^{H_{max}} \sigma_i(H)dH$$

where H_{max} is the maximum field during the measurements. For the CuL^{Et}_2 single crystal, the lower bound on the integration domains of the $\sigma(H)$ curves is set by the value of the critical field H_c. The calculated effective anisotropy fields of the complex are $H_\perp = 1390$ Oe (along *c* axis) and $H_{||} = 420$ Oe (along *a* axis). The anisotropy of magnetic properties in a plane of the polymeric layers (*ab*) is much smaller than that in the perpendicular direction as a consequence of the quasi two-dimensional magnetic system. Thus, the anisotropy observed in CuL^{Et}_2 should be attributed to the "easy plane" type.

The single crystals of copper–3-imidazoline nitroxide complexes CuL^R_2 have similar structures. Also, their ordering temperatures are very close, indicating the same order of exchange interactions (Table 1).

All four complexes cannot be considered together as they have different symmetries. However, pairwise comparison of CuL^{Et}_2, CuL^{Me}_2 and $CuL^{C(O)OEt}_2$, $CuL^{C(O)OMe}_2$ reveals the decrease of the transition temperature on substitution of the methyl group with ethyl. This substitution also results in some elongation of bonds in the coordination environment of copper as well as the increase of interlayer separations (Table 1). Corresponding evolution is found in the mutual orientation of the $\{CuL_2\}$ fragments as can be seen from the angles Cu–O (φ1), Cu–N (φ2), and Cu–O$^{(NO)}$ (φ3) between the *b* axis and the relevant bonds (Table 1). The magnetic behavior of the CuL_2 complexes is significantly different in the magnetically ordered phase. Under the transition temperature $CuL^{C(O)OEt}_2$ and $CuL^{C(O)OMe}_2$ are ferromagnets whereas CuL^{Et}_2 and CuL^{Me}_2 behave as metamagnets. At the same time the critical field of the metamagnetic transition for CuL^{Et}_2 is 3.6 times lower than in isostructural CuL^{Me}_2. The increase of the interlayer separation for CuL^{Et}_2 as compared with that of CuL^{Me}_2 correlates with the decrease of H_c. Assuming that metamagnetism originates from dipole interactions only, the $H_c(CuL^{Me}_2)/H_c(CuL^{Et}_2)$ ratio should be proportional to the $R^3(CuL^{Et}_2)/R^3(CuL^{Me}_2)$ ratio, *R* being an effective distance between magnetic dipoles as measured between copper ions belonging to the adjacent polymeric layers. But this supposition does not hold true. For this reason we suppose that the difference in magnetic properties of the CuL_2 complexes originates from the difference in magnetic anisotropy energy. The comparison of the critical fields and the anisotropy fields within the polymeric layers indicates that a large H_c corresponds to a large $H_{||}$, as sketched in Figure 5.

Table 1. Magnetochemical constants and selected structural data for the CuL_2 polymers.

	CuL^{Me}_2	CuL^{Et}_2	$CuL^{C(O)OMe}_2$	$CuL^{C(O)OEt}_2$
Ordering type	metamagnet	metamagnet	ferromagnet	ferromagnet
T_N (or T_c) [K]	4.9	4.5	5	4.2
H_c [Oe]	1600	440	–	–
$H_\perp$ [Oe]	1340	1390	1100	500
$H_{\|\|}$ [Oe]	670	420	300	200
Symmetry	*Pbca*	*Pbca*	$P2_1/c$	$P2_1/c$
Intralayer (Cu–Cu) [Å]	7.780	7.768	7.786	7.919
Interlayer (Cu–Cu) [Å]	11.869	11.978	11.929	11.939
Cu–N [Å]	2.049	2.046	2.061	2.058
Cu–O [Å]	1.902	1.907	1.913	1.994/1.837
Cu–O$^{(NO)}$ [Å]	2.469	2.582	2.513	2.534
(Cu–O–N) [°]	175.8	160.6	157.9	157.53
φ1 [°]	46.7	79.8	72.6	65.5
φ2 [°]	64.2	35.7	59.8	47.9
φ3 [°]	50.2	61.9	29.6	52.9

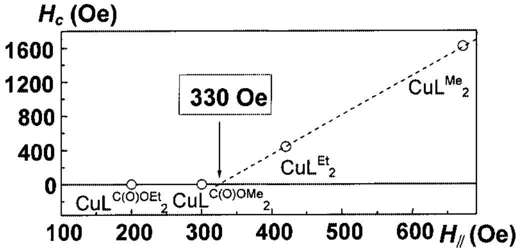

Figure 5. The H_c vs $H_{||}$ plot for the CuL_2 complexes.

The data available are too scarce to deduce the H_c versus $H_{||}$ dependence. However, linear approximation based on CuL^{Me}_2 and CuL^{Et}_2 yields the value 330 Oe for the intercept of $H_{||}$. Following this approximation, the metamagnetic transition does not exist for fields lower than 330 Oe; this conclusion is in agreement with the experimental data. The complexes $CuL^{C(O)OEt}_2$ and $CuL^{C(O)OMe}_2$ fall exactly within this range of the anisotropy field. In contrast to CuL^{Et}_2 and CuL^{Me}_2, the complexes $CuL^{C(O)OEt}_2$ and $CuL^{C(O)OMe}_2$ are monoclinic. Therefore, the free energy of magnetic anisotropy for the latter has a different set of anisotropy constants from that of CuL^{Et}_2 and CuL^{Me}_2. Generally, different values and temperature dependences of anisotropy constants for each type of symmetry can result in the overall stabilization of either the ferromagnetic or the antiferromagnetic ground state.

Conclusion

A novel layered polymeric complex, CuL^{Et}_2, is synthesized and characterized; the complex demonstrates metamagnetic phase transition at 4.5 K. The transition critical field is 440 Oe, corresponding to a magnetic energy of 0.088 K. Below the H_c the antiferromagnetic vector coincides with the *b* axis, and $\chi_\perp$ with the *a* and *c* axes. Above the H_c the easy magnetization axis runs along the crystallographic *b* direction, the hard magnetization axis being orthogonal to the polymeric layers. The onset of metamagnetic transition and the value of the critical field in the series of CuL_2 complexes are attributed to the difference in magnetic anisotropy energy within the polymeric layers of the complexes.

Experimental Section

General Remarks: All the solvents were used as purchased. The nitroxide HL^{Et} was synthesized according to ref.[12].

Synthesis of CuL^{Et}_2: A mixture of $CuCl_2 \cdot 2H_2O$ (55 mg, 0.32 mmol) and HL^{Et} (150 mg, 0.62 mmol) was dissolved in warm ethanol (15 mL). The solution was filtered and the pH adjusted to 8 with aqueous ammonia. In a span of time varying from hours to days, the solution yielded a light-green precipitate, which was collected, washed with ethanol, and recrystallized from boiling ethanol. Yield 105 mg (65%). M.p. 209−212 °C. Calcd. C 54.0, H 6.2, N 15.7; found C 54.1, H 6.4, N 15.7. The crystals of the complex suitable for an X-ray diffraction study and for magnetic measurements were obtained on slow crystallization of the material from ethanol.

X-ray Crystallographic Study: The X-ray single-crystal data for CuL^{Et}_2 were recorded with an Enraf–Nonius CAD4 four-circle diffractometer. The crystallographic data, conditions used for the intensity data collection, and some features of the structure refinement are listed in Table 2.

Table 2. Crystal data and structure refinement for CuL^{Et}_2.

	CuL^{Et}_2
Empirical formula	$C_{24}H_{34}CuN_6O_4$
Formula mass	534.11
Crystal system	orthorhombic
Space group	*Pbca*
a [Å]	10.732(1)
b [Å]	11.233(1)
c [Å]	21.417(4)
V [Å^3]	2581.9(6)
Z	4
T [K]	293(2)
λ(Mo-K_α) [Å]	0.71069
$d_{calcd.}$ [g cm^{-3}]	1.374
μ(Mo-K_α) [mm^{-1}]	0.887
R_1[a] [$I > 2\sigma(I)$]	0.0285
wR_2[b] [$I > 2\sigma(I)$]	0.0553

[a] $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$.

Graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å) with the $\theta/2\theta$ technique was used to collect the data set. The accurate unit-cell parameters were determined from automatic centering of 24 reflections, $10° < \theta < 15°$, and refined by least-squares methods. 1726 reflections were collected in the range $1.90° < \theta < 24.96°$; 1064 reflections were assumed to be observed upon applying the condition $I > 2\sigma(I)$. Corrections were applied for Lorentz polarization effects. The structure was solved by direct methods, using the SIR97[13] program, and refined by full-matrix least-squares method with the SHEXL-97[14] package.

Magnetic Measurements: The magnetochemical experiment was run with an MPMS-5S ("Quantum Design") SQUID magnetometer at temperatures from 2 to 300 K in a homogeneous external magnetic field of up to 49.5 kOe. Magnetic measurements on a single crystal were performed along the crystallographic axes *a*, *b*, and *c*. The relation of the crystal appearance to the crystallographic axes was established by X-ray diffraction. The molar magnetic susceptibility χ of the complexes was calculated 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}. For the paramagnetic region, the effective magnetic moment was calculated by the formula $\mu_{eff} = [(3k/N_A\beta^2)\chi T]^{1/2} \approx (8\chi T)^{1/2}$, 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 magnetic susceptibility on temperature $\partial\chi/\partial T$. The magnetization dependences $\sigma(H)$ of the CuL^{Et}_2 single crystal in the ferromagnetic state were plotted with allowance for the demagnetization field of the sample. The actual field in the crystal was calculated for each direction by the formula $H_i = H - N_i\sigma_i$, where $i = a$, *b*, and *c*; and *N* is the demagnetization factor evaluated using the tables for a disk sample.[15]

CCDC-243550 and -192277 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.

Acknowledgments

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[1] V. I. Ovcharenko, R. Z. Sagdeev, *Russ. Chem. Rev.* **1999**, *68*, 345–363.

[2] E. V. Kuzmin, G. A. Petrakovsky, *Izvestiya Vuzov MV I SSO SSSR, Fizika* **1988**, *3*, 94–101.

[3] A. Caneschi, D. Gatteschi, J. P. Renard, P. Ray, R. Sessoli, *Inorg. Chem.* **1989**, *28*, 1976–1980.

[4] Yu. Shvedenkov, V. Ikorskii, D. Guschin, E. Fursova, V. Ovcharenko, *Polyhedron* **2001**, *20*, 1207–1213.

[5] R. D. Willett, in *Magneto-Structural Correlations in Exchange Coupled Systems* (Eds.: R. D. Willett et al.), D. Reidel Publishing Company, **1985**, pp. 389–420.

[6] A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press, Oxford, **1986**, p. 313.

[7] V. Ovcharenko, A. Burdukov, R. Musin, *Mol. Cryst. Liq. Cryst.* **1995**, *273*, 89–99.

[8] A. F. Stassen, H. Kooijman, A. L. Spec, L. Jos de Jongh, J. P. Haasnoot, J. Reedijik, *Inorg. Chem.* **2002**, *41*, 6468–6473.

[9] J. J. M. Steijger, E. Frikkee, L. J. De Jongh, W. J. Huiskamp, *Physica B* **1984**, *123B*, 271–283.

[10] R. Navarro, in *Magnetic Properties of Layered Transition Metal Compounds* (Eds.: L. J. De Jongh), Kluwer Academic Publishers, Netherlands, **1990**, pp. 105–184.

[11] S. V. Vonsovskii, in *Magnetism* (Ed.: A. A. Gusev), Izdatelstvo "Nauka", **1971**, p. 476.

[12] V. A. Reznikov, I. Yu. Bagryanskaya, Yu. V. Gatilov, *Russ. Chem. Bull.* **2000**, *49*, 899–905.

[13] A. Altomare, M. C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

[14] G. M. Sheldrick, *SHELX–97, Programs for Crystal Structure Analysis* (*Release 97-2*). University of Göttingen, Germany, **1998**.

[15] V. I. Chechernikov, in *Magnitnie izmereniya* (Ed.: E. I. Kondorskii), Izdatelstvo Moskovskogo Universiteta, **1963**, p. 57.

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