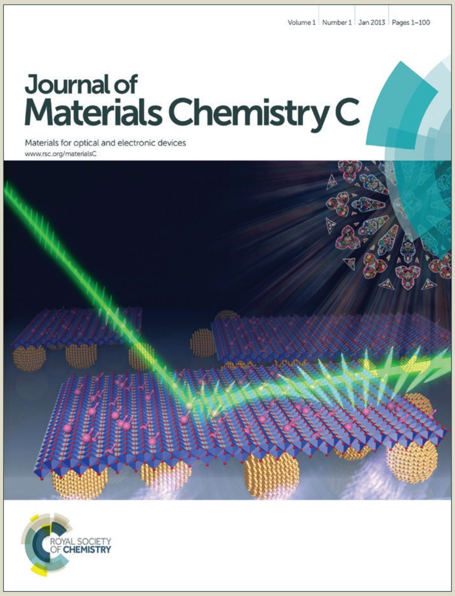
Journal of
Materials Chemistry C

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/materialsC

Journal Name

COMMUNICATION

Heterospin Pressure Sensor

Kseniya Yu. Maryunina,[a] Xiao Zhang,[a] Sadafumi Nishihara,[a] Katsuya Inoue,*[a] Vitaly A. Morozov,[b] Galina V. Romanenko[b] and Victor I. Ovcharenko*[b]

Received xxth April 2015,
Accepted xxth xxx 2015

DOI: 10.1039/x0xx00000x

www.rsc.org/

The effect of the external pressure on the magnetic properties was studied for the first time for heterospin crystals based on the Cu(II) complex with nitroxide $[Cu(hfac)_2NN\text{-}PzMe]$, which exhibits the spin-crossover-like phenomenon. An increase in the hydrostatic pressure to 0.14 GPa caused a significant shift of the magnetic anomaly temperature (from 150 K to 300 K). This complex actually functions as a highly sensitive external pressure sensor.

An active search for molecular magnetic materials of new types whose structure and functional properties can change with temperature, pressure, and magnetic field or under irradiation has been stimulated by the development of fundamental science and high potential for their application.[1-6] The effect of the external pressure on the physicochemical characteristics of multispin compounds remains a promising but least studied field of research. An analysis of the effect of the external pressure on the functional properties of molecular magnets can provide valuable information on the mechanism of the observed phase transitions and serve as a basis for creating new highly sensitive pressure sensors used in cryogenic technology, deep-sea facilities, seismological research and space exploration.[2-6]

Along with growth of interest in materials whose physical characteristics are sensitive to the external pressure, manometers and stress memory detectors of various types formerly having no analogs have increased in number.[2-6] A new promising class of objects of this type may be Cu(II) complexes with nitroxides, which exhibit the spin-crossover-like (SCO-like) phenomenon.[5-17] In the course of a thermally induced structural rearrangement of [Cu(II)–O•–N<] or [>N–•O–Cu(II)–O•–N<] heterospin exchange clusters inside these crystals, the energy of exchange interaction between the odd electrons of the paramagnetic centers changes, leading to anomalies similar to spin transitions on the curve of the temperature dependence of the effective magnetic moment $\mu_{eff}(T)$.[3-5,9] The phase transitions are often accompanied by a pronounced change of color of the compound[13,17] and can occur without decomposition of single crystals despite the significant structural rearrangement of the solid and considerable changes in the volume of both the unit cell and the crystal as a macroobject.[7-9,13-17] It was also shown that the SCO-like phenomenon in these objects can be induced by light at low temperatures (LIESST effect).[18,19] However, the pressure effect on the magnetic properties of compounds from this family was not studied systematically. We actually know of only one study of the pressure effect on the magnetic characteristics of the SCO-like complex of Cu(II) with dinitroxide,[11a] in which the magnetic anomaly was completely suppressed at a pressure of ~0.6 GPa.[11b]

We studied the hydrostatic pressure effect on an abrupt magnetic anomaly of the [Cu (hfac) 2NN-PzMe] heterospin complex (hfac is the hexafluoroacetylacetonate anion, NN-PzMe is 2-(1-methyl-1H-pyrazol-4-yl)-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazole-3-oxide-1-oxyl). Solid $[Cu(hfac)_2NN\text{-}PzMe]$ is formed by polymer chains with a “head-to-tail” motif, in which the nitroxide is coordinated via the O atom of the nitroxyl group and the N atom of the pyrazole ring (Fig. 1).[7-9,1] The abrupt change in μ_{eff} at 145-150 K results from the rearrangement of the CuO_5N Jahn-Teller coordination units, in half of which the Cu-O_{NO} bond length changes drastically from 2.47 Å at 150 K to 1.98 Å at 140 K (Fig. 2, Table 2ESI†).[7-9,15,20] As a result, in half of all [Cu(II)–O•–N<] exchange clusters, the ferromagnetic exchange transforms into strong antiferromagnetic exchange,

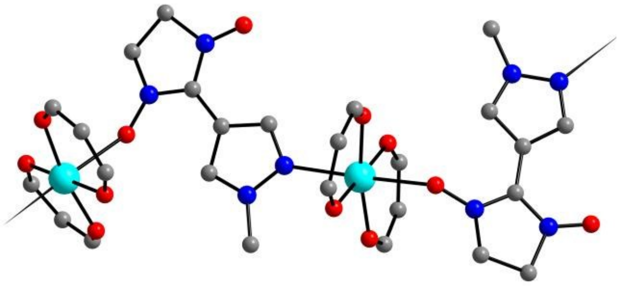


Fig. 1. Fragment of the polymer chain with the “head-to-tail” motif in solid $[Cu(hfac)_2NN\text{-}PzMe]$ (the H atoms, the geminal CH_3 and CF_3 groups are omitted).

---

[a] Department of Chemistry, Graduate School of Science, Center for Chiral Science and Institute for Advanced Materials Research, Hiroshima University, 1-3-1, Kogamiyama, Higashi-Hiroshima, 739-8526, Japan, E-mail: kxi@hiroshima-u.ac.jp

[b] International Tomography Center SB RAS, Institutskaya 3a, Novosibirsk, 630090, Russia. E-mail: Victor.Ovcharenko@tomo.nsc.ru

† Electronic Supplementary Information (ESI) available: Synthetic procedure, full experimental details, and crystallographic data. See DOI: 10.1039/x0xx00000x

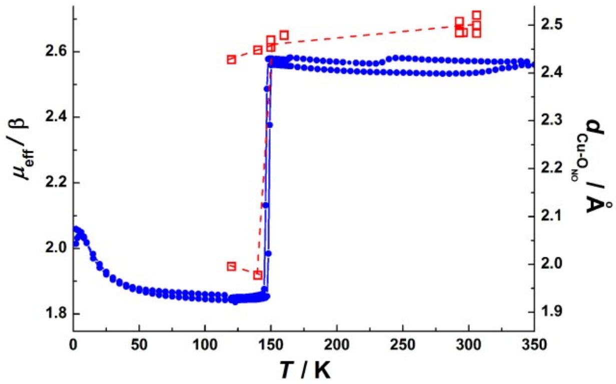


Fig. 2. Temperature dependence of μ_{eff} (-●-) and the Cu-O_{NO} distances (-□-)[7,8,14,15] at 10^{-4} GPa.

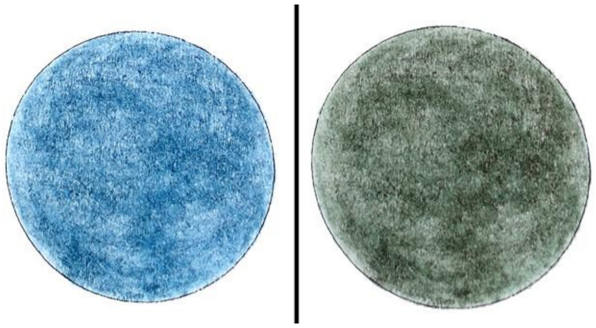


Fig. 3. Thermochromism of the complex: T<80 (left) and T=300 K (right).

which decreases μ_{eff} per single [Cu(hfac)$_2$NN-PzMe] fragment by a factor of √2. In the temperature ranges 235-245 K (on cooling)[7-9,15,20] and 320-350 K (on heating),[20] [Cu(hfac)$_2$NN-PzMe] experienced another transition accompanied by a change in the symmetry (monoclinic–triclinic) and a twofold increase (decrease) of the crystallographically independent fragment of the polymer chain. However, this structural rearrangement did not considerably affect the Cu-O_{NO} distances in the CuO$_5$N coordination units (Table 2ESI†); as a result, the changes on the value of μ_{eff} in the range 230-350 K during the cooling–heating cycle corresponding different polymorph modifications were quite small (Fig. 2).

Also note that the phase transition coupled with the magnetic anomaly in [Cu(hfac)$_2$NN-PzMe] was accompanied by pronounced thermochromism. The heating of finely grinded [Cu(hfac)$_2$NN-PzMe] powder applied to paper and preliminarily cooled with liquid nitrogen led to an abrupt change of its color from dark green to dark blue (Fig. 3). The thermochromism of the heterospin complex in this case serves as an additional indicator of a structural magnetic phase transformation.

Considerable changes in the structure of [Cu(hfac)$_2$NN-PzMe] in the range 145-150 K induced by the repetition of the cooling–heating cycles prompted us to study the response of the solid complex to a change in the external pressure (Fig. 4). At 10^{-4} GPa, the magnetic behavior of the [Cu(hfac)$_2$NN-PzMe] complex placed in a high-pressure cell was the same as the behavior described above for the sample at atmospheric pressure measured under normal conditions. Nevertheless, immersion of the sample in oil as a pressure-transmitting medium led to a certain broadening of the hysteresis loop. A series of experiments showed that an increase in pressure reproducibly caused a considerable increase in the magnetic anomaly temperature (T_a) (Fig. 4). When the pressure increased to a relatively low value, ~0.14 GPa, T_a shifted toward the values exceeding the room temperature. When the pressure increased further to ~0.32 GPa, the compound was in a strongly coupled state over the whole temperature range 2-350 K. At increased pressure, the shape of the transition became smoother and the hysteresis loop width monotonically decreased and became completely degenerate at P > 0.14 GPa (Fig. 4, Table 3ESI†). All the above-described changes in the magnetic properties under the action of pressure were completely reversible. When the pressure decreased to the initial value, the dependence $\mu_{eff}(T)$ acquired the same form as before the pressure increase.

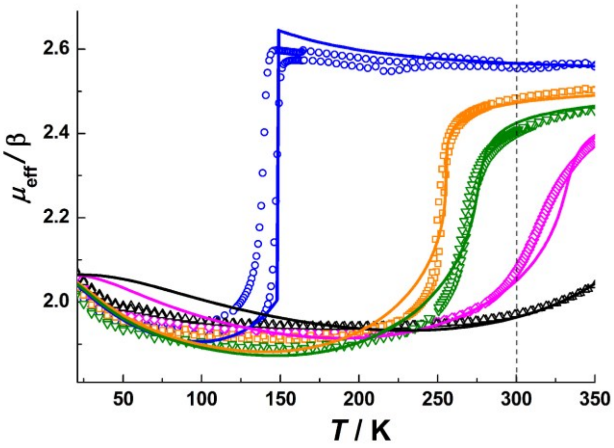


Fig. 4. Experimental dependences of $\mu_{eff}(T)$ for [Cu(hfac)$_2$NN-PzMe] at 10^{-4} (○), 0.04 (□), 0.07 (▽), 0.14(◇), and 0.32 (△) GPa. Solid curves: theoretical fitting of experimental data (Q_1= 7.01, Q_2= 0.0175, J_0= 13 K - blue line; Q_1= 1.05, Q_2= 0.014 J_0= -14 K - orange line; Q_1= 1.33, Q_2= 0.02, J_0=-21 K - green line; Q_1= 0.7, Q_2= 0.024, J_0= -29 K - magenta line; Q_1= 0.56, Q_2= 0.028, J_0=-40 K - black line).

As shown elsewhere,[21] the degree of cooperativity of interactions in a uniform chain of two-spin exchange clusters can be qualitatively expressed as $\varepsilon^2/q \gg |J_0|$, where $\varepsilon = (\partial J/\partial \Delta)|_{J_0}$ is the slope of exchange integral $J(\Delta) = J_0 - \Delta\varepsilon$ under an axial deformation Δ of the exchange cluster, and q is the parameter of the internal elasticity of the exchange cluster. This condition corresponds to the so-called "soft" chain of exchange clusters, for which the temperature of the magnetic structural transition can be specified by the expression: $T_Q \approx -J_0 + \frac{3}{16}\frac{\varepsilon^2}{q}$. Previous successful fitting[21] of the experimental data[7-9,15] (Fig. 2) was based on the fact that the heterogeneous chain consists of alternating exchange clusters of two types with different slope parameters $|\varepsilon_2| \gg |\varepsilon_1|$. The position of the transition temperature T_Q is approximated as $T_{Q_2} \approx -J_0 + \frac{1.8}{16}\frac{{\varepsilon_2}^2}{q}$. The exchange cluster ε_2 is described as "soft" ($Q_2 = 2|J_0|q/{\varepsilon_2}^2 = 0.0175 \ll 1$) and is responsible for the cooperative properties of the heterogeneous chain of exchange clusters. The exchange cluster ε_1 is a "hard" cluster for which $Q_1 = 2|J_0|q/{\varepsilon_1}^2 = 7 \gg 1$, and its thermal deformation is insignificant over the whole temperature range, which agrees well with the X-ray diffraction analysis data.[7-9,15] A physical meaning of the parameters Q_1 and Q_2 is in the following. If $\Delta_{0i} = |J_0/\varepsilon_i|$ is a characteristic length of $J(\Delta)$

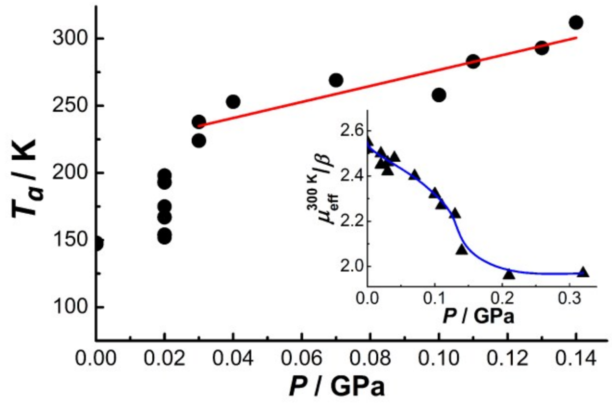


Fig. 5. Pressure dependence of T_a↑: experimental data (●); linear dependence in the pressure range 0.03-0.15 GPa (—). Insert: Pressure dependence of μ_{eff} at 300 K.

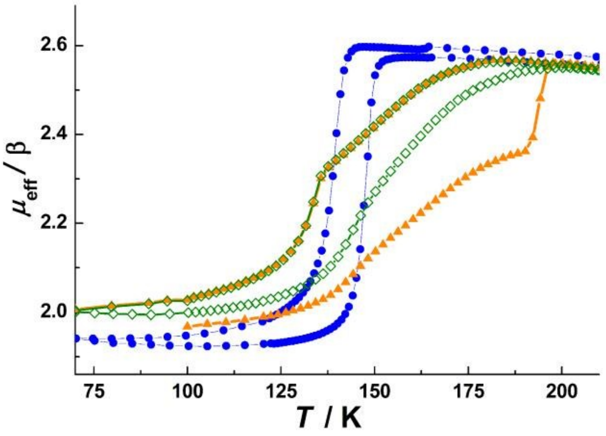


Fig. 6. Dependence of $\mu_{eff}(T)$ at 10^{-4} GPa(-●-) and at a pressure lower than 0.03 GPa: the first (-▲-) and second (-◇-) heating–cooling cycles.

change, then the value $Q_i = 2|J_0|q/\varepsilon_i^2 = 2q\Delta_{0i}^2/|J_0|$ (*i* = 1, 2) is proportional to the ratio of elastic deformation energy of *i*-th exchange cluster on the scale Δ_{0i} .to the value $|J_0|$.

We assume that under external pressure changes in the coordination units would have the same character like it was shown for other copper complexes elsewhere.[6] So under this consideration the distances between paramagnetic centers in the exchange clusters [Cu(II)–O•–N<] should be decreased, leading to a change in the magnitude and sign of the exchange integral J_0. We performed theoretical fitting of the $\mu(T)$ curves at different pressures based on the model,[21-23] which showed good agreement with the experimental data (Fig. 4). An increase in $|J_0|$ at increased pressure led both to a shift of the $\mu(T)$ curves toward higher temperatures and to an increase in $Q_2 = 2|J_0|q/\varepsilon_2{}^2$, i.e., to a weakening of chain cooperativity. Our calculations also showed that the ε_2 and ε_1 values, which nonlinearly affect the corresponding Q_2 and Q_1 parameters, also changed at increased pressure *P*. The relation $Q_1 \gg Q_2$ is still valid, though the Q_2 and Q_1 values evidently became closer. The temperature range of the SCO-like magnetic anomaly is mainly determined by the "soft" exchange clusters ε_2, while the values of $\mu(T)$ below the transition temperature depend on the "hard" exchange clusters ε_1.

The pressure dependence of the transition temperature at 0.03-0.15 GPa is almost linear (Fig. 5). The standard processing of two independent series of experimental data gave a slope of ~590(±100) K·GPa^{-1}, which suggests much higher sensitivity of this compound compared with the majority of previously studied iron complexes that exhibited spin transitions.[3-5,24-26] Because of the extremely high response of T_a of the compound to an increase in the hydrostatic pressure, we encountered the complex problem of calibrating the shift of T_a from the applied pressure already at an early stage of our study.

At pressures lower than 0.03 GPa (more exact evaluation was impossible under the given experimental conditions), the behavior of the complex was difficult to analyze (Fig. 6): the transition became smooth and its range was ~80-200 K. In the first heating–cooling cycle, the hysteresis loop considerably broadened and then narrowed during the repeated cycle. This effect is reproduced at any pressure lower than 0.03 GPa and for [Cu(hfac)$_2$NN-PzMe] batches from different syntheses (Fig. 1ESI†). This behavior of the complex cannot be explained in terms of the above-described theoretical approach. The thermodynamic equilibrium in the solid complex at $P < 0.03$ GPa evidently sets in slowly. It should also be taken into account that the experimental data in the range 100-220 K correspond to solidified Daphne 7373 oil used as a pressure-transmitting medium.[30,31] At pressures higher than 0.03 GPa, the SCO-like phenomenon showed itself at temperatures higher than the solidification temperature of Daphne 7373 and was always recorded in the form of a rather abrupt step. Note that a similar broadening of the hysteresis loop was described for spin-crossover compound dispersed in glassy or semicrystalline matrices.[24] The nonlinear pressure dependence of the spin transition temperature for a number of iron complexes was reported elsewhere.[25-27] Applying of pressure may also cause peculiar changes in the structure of compounds, such as the appearance of intermediate phase, which could be quite differ from thermally induced structure rearrangements.[28,29]

In discussing the effect of pressure on the magnetic properties of [Cu(hfac)$_2$NN-PzMe] it should be noted that since the changes at the curve $\mu_{eff}(T)$ in the temperature range 230-350 K are very small, we could not reliably estimate the influence of pressure on this anomaly by magnetic measurements, and therefore did not analyze them. In order to clarify the details and understand the mechanism of the effect of pressure on the magnetic properties and structural transformations in the [Cu(hfac)$_2$NN-PzMe], we are planning to carry out a number of special studies. Crystal structure determination, EXAFS, UV-*viz* and IR spectroscopy study, investigation by EPR method under applied pressure and, if possible, in various temperature ranges would allow us to gain a deeper understanding of this phenomenon.

Conclusions

The data presented here are the first steps in studies of the pressure effect on the SCO-like phenomenon in Cu(II)-nitroxide complexes. Nevertheless, already at this stage it is evident that [Cu(hfac)$_2$NN-PzMe] is a promising candidate for creating highly efficient pressure sensors. The sensitivity of the heterospin complex is approximately one order of magnitude higher than for the majority of classical Fe-containing compounds that show spin transitions.[3-5, 25-29] The shift of the magnetic anomaly temperature (T_a) to ambient temperature occurs at relatively low applied pressures of ~0.14 GPa, which can be reached even in the Earth crust (for example, the hydrostatic pressure at a depth of 5 km in the ocean is ~0.05 GPa; the rock pressure 0.05 GPa is reached under a layer ~2 km thick). In addition, studies of the effect of pressure on the magnetic properties and structure of copper nitroxide complexes can give valuable information for evaluating the so-called “chemical pressure” (modification of substituents in organic ligands, introduction of solvate molecules and other space fillers) when developing the chemical methods for changing the functional properties of SCO-like materials.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (S) (No. 25220803) "Toward a New Class Magnetism by Chemically-Controlled Chirality", Project to Support Female Researchers at Hiroshima University, and Program 2, III-I-83.

Notes and references

1 *Multifunctional Molecular Materials*, ed. L. Ouahab, Pan Stanford Publishing Pre. Ltd., 2013.
2 S. A. Moggach, S. Parsons, in *Spectroscopic Properties of Inorganic and Organometallic Compounds*, ed.: J. Yarwood, R. Douthwaite, S. Duckett, RCS: Cambridge, UK, 2009, vol. 40, pp. 324-354.
3 O. Sato, J. Tao, Y.-Z. Zhang, *Angew. Chem. Int. Ed.* 2007, **46**, 2152 – 2187.
4 J. Linares, E. Codjovi, Y. Garcia, *Sensors* 2012, **12**, 4479-4492.
5 P. Gütlich, V. Ksenofontov, A. B. Gaspar, *Coord. Chem. Rev.* 2005, **249**, 1811-1829.
6 M. A. Halcrow, *Chem Soc. Rev.* 2013, **42**, 1784-1795.
7 P. Rey, V. I. Ovcharenko, in *Magnetism: Molecules to Materials*, IV, eds: J. S. Miller, M. Drillon, Wiley-VCH: New York, 2003, pp. 41-63.
8 V. I. Ovcharenko in *Stable Radicals: Fundamentals and Applied Aspects of Odd-Electron Compounds*, ed. R. Hicks, Wiley-VCH: New York, 2010, pp. 461-506.
9 *Spin-Crossover Materials: Properties and Applications*, ed. M. A. Halcrow, Wiley-VCH: Weinheim, 2013.
10 F Lanfranc de Panthou, E. Belorizky, R. Calemczuk, D. Luneau, C.; Marcenat, E. Ressouche, P. Turek, P. Rey, *J. Am. Chem. Soc.* 1995, **117**, 11247-11253.
11 (*a*) K. Inoue, F. Iwahori, H. Iwamura, *Chem. Lett.* 1998, 737-738. (*b*) Y. Hosokoshi, K. Suzuki, F. Iwahori, K. Inoue, *Annual Rev. of IMS (Institute for Molecular Science)*, 2001, 113.
12 A. Caneschi, P. Chiesi, L. David, F. Ferraro, D. Gatteschi, R. Sessoli, *Inorg. Chem.* 1993, **32**, 1445-1453.
13 M. Baskett, P. M. Lahti, A. Paduan-Filho, N. F. Oliveira Jr., *Inorg. Chem.* 2005, **44**, 6725-6735.
14 A. Okazawa, D. Hashizume, T. Ishida, *J. Am. Chem. Soc.* 2010, **132**, 11516-11524.
15 S. Fokin, V. Ovcharenko, G. Romanenko, V. Ikorskii, *Inorg. Chem.* 2004, ***43***, 969-977.
16 E. Tretyakov, G. Romanenko, S. Veber, M. Fedin, A. Polushkin, A. Tkacheva, V. Ovcharenko, *Aust. J. Chem.*, http://dx.doi.org/10.1071/CH14422.
17 E. V. Tretyakov, S. E. Tolstikov, A. O. Suvorova, A. V. Polushkin, G. V. Romanenko, A. S. Bogomyakov, S. L. Veber, M. V. Fedin, D. V. Stass E. Reijerse, W. Lubitz, E. M. Zueva, V. I. Ovcharenko, *Inorg. Chem.* 2012, **51**, 9385-9394.
18 M. V. Fedin, S. L. Veber, R. Z. Sagdeev, V. I. Ovcharenko, E. G. Bagryanskaya, *Russ. Chem. Bull.* 2010, **59**, 1065-1079.
19 M. Fedin, V. Ovcharenko, R. Sagdeev, E. Reijerse, W. Lubitz, E. Bagryanskaya, *Angew. Chem. Int. Ed.* 2008, **47**, 6897-6899.
20 CCDC 1053800-1053804 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. See DOI: xxx
21 V. Morozov, N. Lukzen, V. Ovcharenko, *Phys. Chem. Chem. Phys.* 2010**, 12,** 13667-13673.
22 V. A. Morozov, N. N. Lukzen, V. I. Ovcharenko, *Dokl. Phys. Chem.* 2010, **430**, Part 2, 33-35.
23 V. A. Morozov, *J. Struct. Chem.*, 2014, **55**, 1033-1038.
24 A. Tissot, C. Enachescu, M.-L. Boillot, J. Mater. Chem., 2012, **22**, 20451-2045724A.
25 G. G. Levchenko, V. Ksenofontov, A. V. Stupakov, H. Spiering, Y. Garcia, P. Gütlich, *Chem. Phys.* 2002, **277**, 125-129.
26 A. Galet, A. B. Gaspar, M. C. Muñoz, G. V. Bukin, G. Levchenko, J. A. Real, *Adv. Mater.* 2005, **17**, 2949-2953.
27 Galet, A. B. Gaspar, M. C. Muñoz, G. Levchenko, J. A. Real, *Inorg. Chem.* 2006, **45**, 9670-9679.
28 H. J. Sheperd, S. Bonnet, P. Guionneau, S. Bedoui, G. Garbarino, W. Nicolazzi, A. Bousseksou, G. Molnár, *Phys. Rew. B*, 2011, **84**, 144107(7).
29 H. J. Sheperd, P. Rosa, L. Vendier, N. Casati, J.-F. Létard, A. Bousseksou, P. Guionneau, G. Molnár, *Phys. Chem. Chem. Phys.* 2012**, 14,** 52650-5271.
30 X. Wang, K. V. Kamenev, *Low Temp. Phys.*, 2014, **40**, 735-746.
31 K. Murata, H. Yoshino, H. O. Yadav, Y. Honda, N. Shirakawa, *Rev. Sci. Instrum.* 1997, **68**, 2490-2493.

Table of contents entry

The spin transition temperature of the Cu(II)-nitroxide complex was found to shift by approximately 100 K toward higher temperatures when the hydrostatic pressure increased to ~0.04 GPa.