Levamisole Based Co(II) Single-Ion Magnet

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A new Co(II) complex, $[Co(NCS)_2(L)_2]$ (**1**) has been synthesized based on levamisole (L) as a new ligand. Single-crystal X-ray diffraction analyses confirm that the Co(II) ion is having a distorted tetrahedral coordination geometry in the complex. Notably strong intramolecular S···S and S···N interactions has been confirmed by employing Quantum Theory of Atoms in Molecules (QTAIM). These intramolecular interactions occur among the sulfur and nitrogen atoms of the levamisole ligands and also the nitrogen atoms of the thiocyanate. Direct current (dc) magnetic analyses reveal presence of zero field splitting (ZFS) and large magnetic anisotropy on Co(II). Detailed *ab initio* ligand field theory calculations quantitatively predicted the magnitude of ZFS. Prominent field-induced single-ion magnet (SIM) behavior was observed for **1** from dynamic magnetization measurements. Slow magnetic relaxation follows an Orbach mechanism with the effective energy barrier $U_{eff} = 29.6$ (7) K and relaxation time $\tau_o = 1.4\ (4) \times 10^{-9}$ s.

Introduction

In the last decade, significant effort has been made to design and prepare single molecule magnets (SMMs). SMMs has shown huge potential for the data storage, quantum computing, and memory devices applications.[1] Large spin ground state and high magnetic anisotropy are the imperative factor for poly-nuclear complexes or clusters to design SMMs. There are number of SMMs have been reported so far, but low magnetic blocking temperature (T_B) and low effective energy barrier restrict their applicability for material application.[2] Now the research interest has been shifted noticeably from designing magnetic polynuclear to mononuclear complexes, called as Single-ion magnets (SIMs), for last couple of years. From the literature it is evident that together large ground spin state and high magnetic anisotropy cannot be always achievable in the multinuclear complex system.[2,3] Therefore, SIMs are becoming the research hotspot in the field of molecular magnetism as it could address the problem associated with typical SMMs.[4]

In SIMs, spin-orbit coupling of metal ions largely contributes to magnetic anisotropy of the system. So, ligand strength and coordination geometry are the two important factors that must be kept in consideration for designing the SIMs.[5]

Till now, some excellent lanthanide-based SIMs have been reported.[6] But research interest is also some extent inclined towards the designing of 3*d*-SIMs due to high ligand field effect, tendency to form low coordination number and higher stability of 3*d* complexes.[3,7]

Among the 3*d*-SIMs, the Co (II) complexes claim the majority stake due to the non-integer spin ground state ($S = 3/2$) and high magnetic anisotropy. So far, several mononuclear Co (II) complexes have been reported with excellent single ion magnet properties.[3g,8] Generally, the coordination number of Co(II) ions varies from two to six in most of the reported mononuclear Co(II) complexes.[3g,8] It has been observed that mononuclear Co(II) complexes with two, three, four and six coordination number exhibit very good single ion magnet behavior.[4c]

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It should be noted that most of the SIMs that are based on two-coordinate Co(II) have low thermal stability and are highly sensitive to air and moisture.[4c] As a result, the practicality of using such complexes in device fabrication could be limited. On the other hand, tetrahedral four-coordinated Co(II) complexes could show great potential as these complexes have not only good magnetic properties but also, they are robust and have good air and moisture stability.[4c,9]

So, four-coordinate Co(II)-mononuclear complexes as single ion magnets must be a prominent point of interest in this regard. Now the choice of ligand to design such system is also an important aspect. Because the nature of the coordinating ligands largely moderates the magnitude and sign of *D* of Co(II)-ion.[8] Sulfur containing monodentate ligand as N donor could be an interesting pick for design strategy. Several mononuclear tetrahedral Co(II) single molecule magnets with four nitrogen (N4) coordination have been reported till date.[3g] But ligands with open sulfur atom could be useful for surface application of SMMs.[1] So, in this regard, we choose levamisole as a ligand to prepare Co(II) based mononuclear complex as single ion magnets.

In this work, we report the crystal structure and magnetic properties of new Co(II) mononuclear complex with levamisole ligand. Structural characterization by *X*-ray crystallography reveals that the Co(II) is having distorted tetrahedral geometry. Detailed quantum chemical approach has been taken to analyze the intramolecular S···S and S···N interactions which is found to be the strongest one stabilizing the complex molecule in the crystal structure. Detailed magnetic study shows presence of ZFS and magnetic anisotropy with magnetic-field-dependent single ion magnetic (SIM) behavior. The magnitude of ZFS is quantitatively estimated by *ab initio* ligand field theory calculations.

Results and Discussion

Structural Description of 1

Low-temperature single-crystal *X*-ray diffraction studies revealed that **1** crystallizes in monoclinic system with space group $P2_1$. The crystallographic data of **1** are summarized in Table S1. The asymmetric unit of the crystal contains one molecule of **1** (Figure 1). The Co(II) ion is having a tetrahedral N4 coordination environment (Figure 1). Two nitrogen donor atoms from two levamisole and other two nitrogen atoms from two thiocyanate ligands are coordinating to the Co(II) central atom (Figure 1). In order to get more understanding, continuous shape measures (CShMs) have been done on this complex by using SHAPE 2.1 program.[10] The results confirm that the coordination environment of Co(II) ion is having a decent deviation from ideal tetrahedral geometry with minimum CShM value of 0.228 (Table S2).

The Co–N bond distances of **1** are in the range of 1.973(4)–1.997(3) Å. The bond angle N–Co–N with two levamisole ligands and two thiocyanates are 108.60° and 112.65° respectively. The two N–Co–N planes from levamisole and isocyanate are in near orthogonal position with a dihedral angle of 87.88°, (Figure S1). The closest distance between two Co(II) ions in the crystal lattice is 8.376 Å.

Also, weak sulfur (S)···sulfur (S) interactions and π–π interactions has been observed among levamisoles and thiocyanates (Figure S2). These noncovalent interactions facilitate the formation of pseudo two-dimensional supramolecular arrangement for **1** along *ac*-plane in crystal packing. Now, the remarkable features of this crystal structure of **1** are the strong intramolecular S···S and S···N interactions among the sulfur and nitrogen atoms of the levamisole ligands (d(S1···S2) = 3.756(1) Å, d(S1···N2) = 3.505(3) Å), and also nitrogen atom of the thiocyanate group (d(S2···N4) = 3.432(4) Å). To investigate the nature of these interactions we employed Quantum Theory of Atoms in Molecules (QTAIM)[11] calculations performed by Multiwfn[12,13] software. For visualization of the calculated properties, the AIMAll software was used.[14] To obtain wavefunctions, the

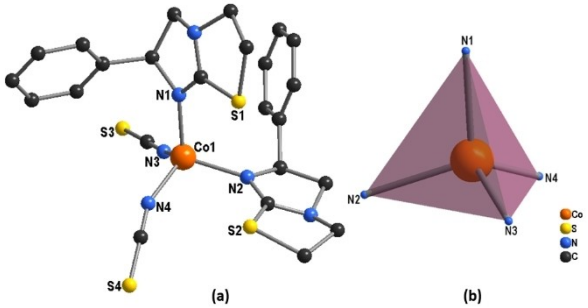

Figure 1. (a) Molecular structure of **1**; hydrogen atoms have been omitted for clarity (b) Polyhedral representation of the coordination environment around the Cobalt (II) center.

Density Functional Theory (DFT) calculations were used by using Orca 4.2.1 package.[15] To obtain reliable positions of the hydrogen atoms, the Hirschfeld refinement was implemented[16] in NoSpherA2 module[17] of Olex2 (B3LYP level of theory, def2-SVP). The final crystal structure resulting from this refinement was then used as the source of coordinates for subsequent calculations.[18] The obtained results revealed that the aforementioned interactions exhibit bond paths and (3,–1) bond critical points (BCP, Figure 2). The values of $\nabla^2\rho(\boldsymbol{r})$ and $h_e(\mathbf{r})$ calculated at BCPs are both positive ($h_e(\mathbf{r})$ is full energy density), indicating their fully non-covalent nature. The strength of these interactions (E_{int}) can be estimated using a well-established relationship approximated as $E_{int} = V(\mathbf{r})/2$, where $V(\mathbf{r})$ represents the potential energy density.[19] We found that these interactions belong to the strongest intramolecular interactions stabilizing the complex molecule in the crystal structure of **1** (in kJ/mol, E_{int}(S1···S2) = 2.99, E_{int}(S1···N2) = 3.70 and E_{int}(S1···N4) = 4.04). Another intramolecular interaction of comparable strength is represented by a weak C2-H2···N3 hydrogen bonding (E_{int}-(H2···N3) = 5.67 kJ/mol).

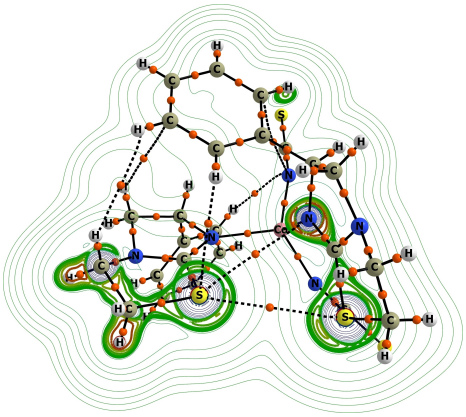

Figure 2. The $\nabla^2\rho(\boldsymbol{r})$ contour plot of the mean squared plane passing through the sulfur atoms of both levamisole ligands and one of their donor nitrogen atom. Orange dots represent (3,–1) bond critical points, black solid lines represent covalent bond paths and black dashed lines represent bond paths of non-covalent interactions. Negative $\nabla^2\rho(\boldsymbol{r})$ regions are depicted with thick contours whereas positive regions are depicted with thin lines.

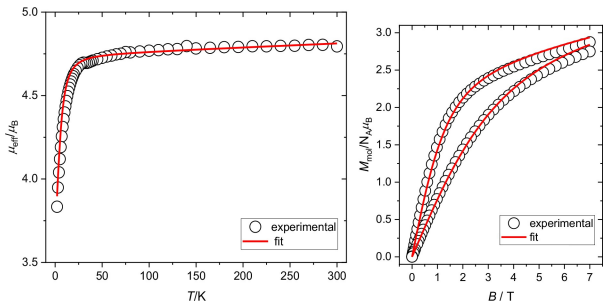

Figure 3. Temperature dependence of μ_{eff}/μ_B measured under the static external magnetic of 0.1 T (left) and field dependence of molar magnetisation measured at 2 and 5 K (right) for **1**. Empty circles represent experimental data, red line fit to eq. 1–3.

Magnetic Properties

All the magnetic measurements were performed on polycrystalline samples. The phase purity of bulk samples of **1** was confirmed by collecting the powder *x*-ray diffraction patterns (Figure S3). From direct current (DC) magnetic susceptibility measurements, the obtained μ_{eff}/μ_B value (μ_{eff} = effective magnetic moment) is 4.81 at room temperature (Figure 3). This value is quite higher than the spin-only value (3.87, $S = 3/2$, $g = 2.00$) of isolated high spin Co(II) ion.[20] Such a high value of μ_{eff} confirms significant orbital contribution to magnetic moment of magnetically anisotropic Co(II) ions.[21] The observed μ_{eff} value decreases slowly with lowering the temperature up to 30 K, then μ_{eff} decreases rapidly to reach a value of 3.83 μ_B at 2 K. This rapid decrease in μ_{eff} at lower temperatures can be explained by the presence of zero field splitting (ZFS) and large magnetic anisotropy, since the shortest distance between two nearby Co(II) ions is 8.37 Å and magnetic exchange interactions are unlikely to be of significant strength.

At low temperatures, the magnetization of **1** shows a sharp increase with increasing magnetic field up to 2.3 T, then gradual increase in magnetization was observed up to the highest experimental field of 7 T without any sign of complete saturation (Figure 3 and S4). The magnetization value at 2 K and 7 T were found to be 2.9 $N\mu_B$. This magnetization value is lower than the theoretical M_{sat} value of 3.0 $N\mu_B$ for an isotropic Co(II) ion ($S = 3/2$). This is due to the high magnetic anisotropy and crystal-field effects in the complex. Also, for reduced magnetization plot, all the magnetization curves do not collapse on the same master curve further indicates the existence of magnetic anisotropy (Figure S4). Therefore, we fitted both datasets of temperature and field dependence with following spin Hamiltonian including ZFS terms *D* (axial magnetic anisotropy parameter) and *E* (rhombic magnetic anisotropy parameter):

$$\hat{H} = \sum_i D_i\left(\hat{S}_{z,i}^2 - \hat{S}_i^2/3\right) + E_i\left(\hat{S}_{x,i}^2 - \hat{S}_{y,i}^2\right) + \mu_B B g_i \hat{S}_{a,i} \quad (1)$$

together with Zeeman term defined in direction of magnetic field as $B_a = B(\sin(\theta)\cos(\varphi), \sin(\theta)\sin(\varphi), \cos(\theta))$ with the help of the polar coordinates. The molar magnetization in *a*-direction of magnetic field B_a was numerically calculated for partition function *Z* built from the energy levels of the spin Hamiltonian as follows:

$$M_a = N_A kT \frac{d\ln Z}{dB_a} \quad (2)$$

Then, the averaged molar magnetization of the powder sample was calculated as the orientational average:

$$M_{mol} = \frac{1}{4\pi}\int_0^{2\pi}\int_0^{\pi} M_a \sin\theta d\theta d\varphi \quad (3)$$

The results of simultaneous fitting of temperature and field dependencies are shown in Figure 3. Reasonable parameters

were obtained only in the case of the positive D parameter (+ 6.4 cm^{-1}) and with rather high rhombicity ($E/D = 0.24$). The attempts to fit the magnetic data with negative D yielded $E/D > 1/3$ and therefore, they cannot be accepted.[22]

To support analysis of experimental magnetic data we performed complete active space self-consistent field (CASSCF) method with a 7-electron in 5-orbital active space (CAS(7,5)), which corresponds to the Co(II) $3d^7$ electron configuration. The dynamic electron correlation was treated by performing the N-electron valence perturbation theory (NEVPT2) method.[23] The energy of the active metal d-orbitals was calculated using the AILFT (*Ab Initio* Ligand Field Theory) module in ORCA 4.2.1. The calculations were done the def2-TZVP basis set for all atoms except for H and C, where less expensive def2-SVP was chosen.[24] Additionally, a def2-TZVP/C auxiliary basis set, for correlation fitting, and chain-of-sphere approximation (RIJCOSX) were utilized.[25] The calculations revealed that the splitting of the ground atomic term ^4F in the ligand field of complex **1** resulted in seven $^4\Gamma$ ligand field terms (LFT). The first excited LFT has energy of 3893 cm^{-1}, which ensures the use of spin Hamiltonian formalism.[26] The energy of the active metal *d*-orbitals was calculated using *ab initio* ligand field theory (AILFT), and the splitting of the d-orbitals closely resembles the characteristic splitting of tetrahedral complexes, which is consistent with the low distortion of the tetracoordinate coordination polyhedron in **1**. The calculated D parameter is negative (−9.5 cm^{-1}) with very low rhombicity ($|E/D| = 0.02$). The calculated magnetic anisotropy easy axis (depicted as D_z tensor axis) is shown in Figure 4. In summary, the *ab initio* calculations quantitatively predicted the magnitude of ZFS quite accurately. However, they did not achieve qualitative agreement, as the predicted D parameter has the opposite sign compared to the experimentally obtained value. Nevertheless, it must be noted that this situation is not unique, as magnetic data fitting is less sensitive to the sign of the D parameter [7h]compared to other methods such as high-field high-frequency electron paramagnetic resonance (HF-EPR), which also can result in strongly correlated values of the g-tensor and E/D values for complexes with large E/D value. [7i] Remarkably, the results of fitting of the dc magnetic data yielded a large E/D value (0.24), effectively producing molar magnetization close to the axial nature (even for $D > 0$).[21b]

To investigate the magnetic dynamics of **1**, alternating current (AC) magnetic susceptibility measurements have been done in the frequency range of 0.1 Hz to 1500 Hz without any external magnetic field. Frequency dependent signal was not observed for out-of-phase ac susceptibilities might be due to quantum tunnelling of magnetization (QTM) by thermal relaxation between the $\pm 3/2$ sublevels.[27] Here, it is important to note that for a $S = 3/2$ system with negative D value, the QTM cannot be always attributed to transverse anisotropy through mixing of wave functions of $\pm M_s$ sublevels for the parity effects.[5f,28] So the hyperfine and dipolar dipole-dipole interactions might be the reason for the QTM.[5f,28]

To suppress this QTM, ac magnetic susceptibility measurements were performed under applied dc magnetic field in the range 0–0.5 T (Figure. S5). **1** exhibit single-channel relaxation under the applied DC field. Therefore, in-phase (χ') and out-of-phase (χ'') components of AC susceptibility were simultaneously fitted to extended one-set Debye model (equations S1, S2). The evaluation of field-dependent relaxation time τ is shown on Figure 5. **1** shows one longest relaxation at 0.3 T (60 Hz, $\tau_{max} =$ 2.6(4) ms) and τ vs. B dependency was successfully fitted to a relaxation equation (4) which involves direct and Raman relaxation processes.

$$\frac{1}{\tau} = AB^m T + d\left(\frac{1 + eB^2}{1 + fB^2}\right)T^n \quad (4)$$

The fits were performed with fixed Raman and direct exponents to theoretical values $m = 4$ and $n = 9$, expected for Kramers ions.[29] Table S3 presents obtained parameters b_1, b_2 (quantum tunnelling), A (direct process) and d, e, f (Raman process).

Further temperature-dependent dynamic magnetic investigations, performed at a 0.2 T DC magnetic field, revealed frequency-dependent peak maxima in the out-of-phase AC susceptibility component, reflecting the characteristic feature of field-induced SIMs. (Figure 6). The ac susceptibility data was fitted with generalized Debye model.[30] The Cole-Cole plot has been represented as Figure 7. The α values were found to be within the ranges of 0.03–0.08, which intitles narrow distribution of magnetic relaxation in the low-temperature region

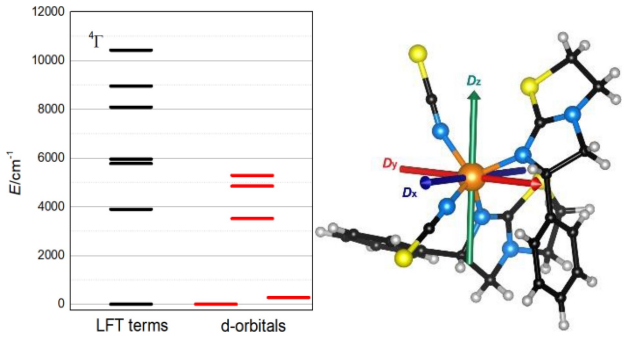

Figure 4. *Left*: *Ab initio* energy of first seven LFT terms (black lines, left) and d-orbitals (red lines, right). *Right:* Molecular structure of **1** overlaid with the D-tensor axes (D_x: blue, D_y: red, D_z: green)

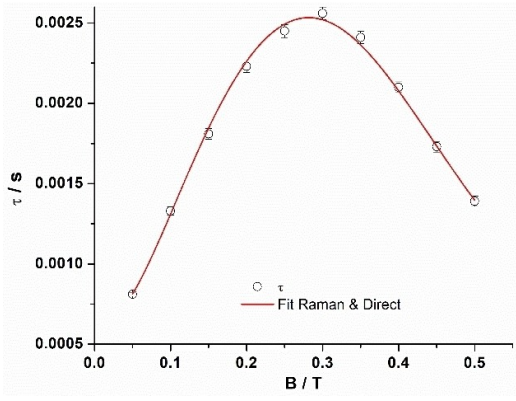

Figure 5. τ vs B dependency of **1**. (Solid red lines represent the fit.)

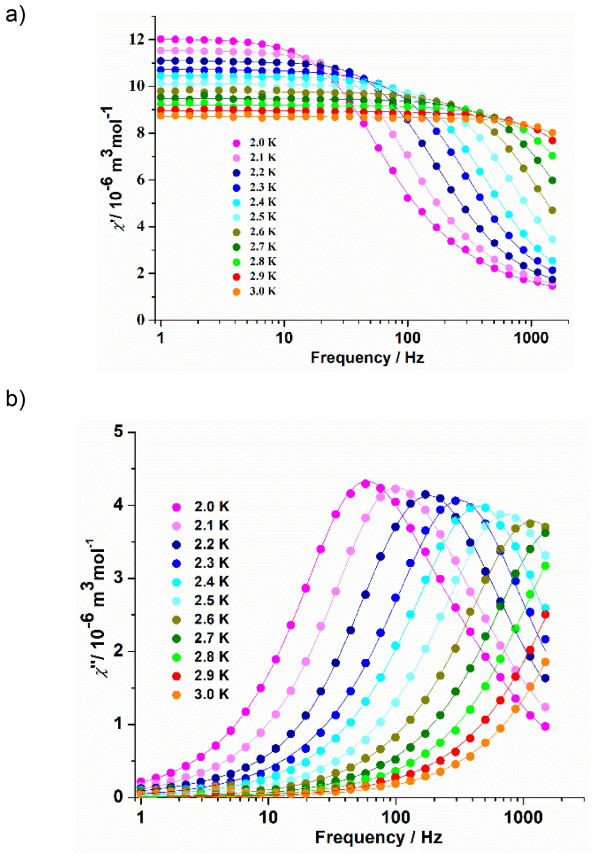

Figure 6. (a) In-phase and Out-of-phase (b) components of the AC magnetic susceptibility for **1** under 0.2 T DC field. (Solid lines represent the fit.)

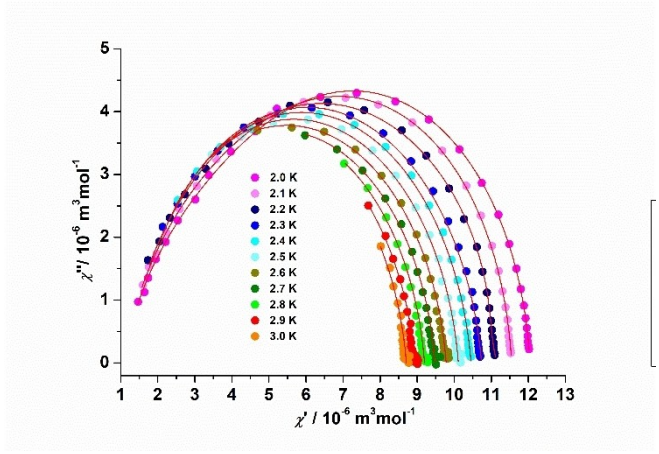

Figure 7. Cole-Cole plots for **1** at different temperatures. (Solid red lines represent the fit.)

(Table S4). By using equation 5, the temperature dependence of the magnetic relaxation time was fitted by considering only thermally assisted Orbach mechanism (Figure 8).

$$ln(1/\tau) = ln(1/\tau_0) - U_{eff}/kT \quad (5)$$

where k is the Boltzmann constant and $1/\tau_0$ is the pre-exponential factor. A linear fit has been obtained and the values

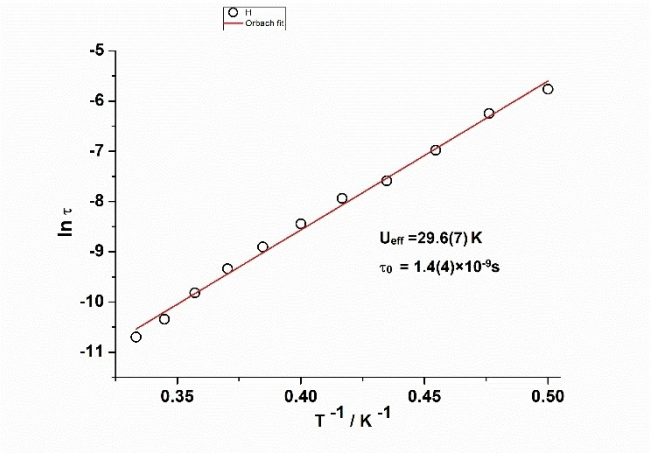

Figure 8. Temperature dependence of relaxation time for **1** with Orbach relaxation process. (Solid red lines represent the fit.)

of effective energy barrier (U_{eff}) is 29.6(7) K and τ_0 is $1.4(4)\times10^{-9}$ s. These fitting parameters are consistent with a typical SIM behavior for Co(II) mononuclear complexes.[3g,20] It's noteworthy that obtained values of U_{eff} are closely aligned with the theoretical ones ($U = 18.4$ K and $U = 27.4$ K) calculated using the equation for Kramer's ions, $U = (S^2 - 1/4)|D|$, with the experimental and calculated axial ZFS parameters, respectively.

Conclusions

In this work, we introduce a new mononuclear Co(II) complex that exhibits field-induced SIM behavior. The synthesis involves the use of levamisole, a sulfur-riched nitrogen donating ligand, to offer distorted tetrahedral coordination geometry for Co(II). The complex contains strong intramolecular S···S and S···N interactions, as confirmed by QTAIM calculations. The Co(II) center of this complex possesses zero field splitting (ZFS) and large magnetic anisotropy. Detailed *ab initio* ligand field theory calculations along with CASSCF/NEVPT2 method quantitatively estimate the magnitude of ZFS. Also, this complex displays prominent field-induced slow relaxation of magnetization with the Orbach process. Based on the overall magnetic properties, this complex can be considered as a typical mononuclear SMM. Therefore, it can be anticipated that combining Co(II) with levamisole as a ligand can create fascinating molecular magnets that might have potential worthiness for surface studies of SMMs as well as understanding magnetic dynamics of complex molecular systems.

Supporting Information

The authors have cited additional references within the Supporting Information. Supporting Information contains synthesis, details of magnetic measurements, single *X*-ray crystallography and *X*-ray powder diffraction.

Acknowledgements

SB thanks Dr. Vishwanath Karad MIT World Peace University and CEITEC for support. IS gratefully acknowledges the financial support of "Large Project for Excellent Researchers" (Nr. 09I03-03-V03-00029). IS also acknowledges the Slovak (Slovak Research and Development Agency: APVV-19-0087, APVV-22-0172, DS-FR-22-0010 and Scientific Grant Agency of the Ministry of Education of Slovak Republic VEGA 1/0029/22) and Czech (Grant Agency of the Czech Republic No. 22-23760S) grant agencies for the financial support. PN acknowledges funding from the EXPRO grant of the Grant Agency of the Czech Republic (GACR 21-20716X)

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: Single ion magnet · Cobalt(II) ion · Levamisole · Magnetic anisotropy · *ab initio* calculations

[1] a) M. M. Affronte, F. Troiani, in *Molecular Magnets: Physical Applications* Eds.: J. Bartolome, J. Luis, F. Fernandez), Springer, Heidelberg, **2014**, 249–273; b) J. M. Zadrozny, J. Niklas, O. G. Poluektov, D. E. Freedman, *ACS Cent. Sci.* **2015**, *1*, 488; c) D. Stepanenko, M. Trif, D. Loss, *Inorg. Chim. Acta.* **2008**, *361*, 3740; d) M. N. Leuenberger, D. Loss, *Nature* **2001**, *410*, 789; e) L. Bogani, W. Wernsdorfer, *Nat. Mater.* **2008**, *7*, 179; f) A. Gaita-Ariño, F. Luis, S. Hill, E. Coronado, *Nat. Chem.* **2019**, *11*, 301; g) D. Aravena, E. Ruiz, *Dalton Trans.* **2020**, *49*, 9916; h) L. Bogani, L. Cavigli, M. Gurioli, R. L. Novak, M. Mannini, A. Caneschi, F. Pineider, R. Sessoli, M. Clemente-Leon, E. Coronado, *Adv. Mater.* **2007**, *19*, 3906; i) M. Mannini, F. Pineider, P. Sainctavit, L. Joly, A. Fraile-Rodriguez, M. Arrio, C. Moulin, W. Wernsdorfer, A. Cornia, *Adv. Mater.* **2009**, *21*, 167; j) M. Mannini, F. Pineider, C. Danieli, F. Totti, L. Sorace, P. Sainctavit, M.-A. Arrio, E. Otero, L. Joly, J. C. Cezar, A. Cornia, R. Sessoli, *Nature* **2010**, *468*, 417.

[2] a) M. Feng, M. L. Tong, *Chem. Eur. J.* **2018**, *24*, 7574; b) G. A. Craig, M. Murrie, *Chem. Soc. Rev.* **2015**, *44*, 2135; c) A. Dey, P. Kalita, V. Chandrasekhar, *ACS Omega* **2018**, *3*, 9462; d) M. Georgiev, H. Chamati, *ACS Omega* **2022**, *7*, 42664; e) A. Z. Lekuona, J. M. Seco, E. Colacio, *Coord. Chem. Rev.* **2021**, *441*, 213984.

[3] a) Y.-S. Meng, S.-D. Jiang, B.-W. Wang, S. Gao, *Acc. Chem. Res.* **2016**, *49*, 2381; b) J. M. Frost, K. L. M. Harriman, M. Murugesu, *Chem. Sci.* **2016**, *7*, 2470; c) A. Borah, R. Murugavel, *Coord. Chem. Rev.* **2022**, *453*, 214288; d) R. Boča, C. Rajnák, *Coord. Chem. Rev.* **2021**, *436*, 213808; e) Y. S. Ding, Y.-F. Deng, Y.-Z. Zheng, *Magnetochemistry* **2016**, *2*, 40; f) J. Liu, Y. C. Chen, J. L. Liu, V. Vieru, L. Ungur, J. H. Jia, L. F. Chibotaru, Y. Lan, W. Wernsdorfer, S. Gao, X. M. Chen, M. L. Tong, *J. Am. Chem. Soc.* **2016**, *138*, 5441; g) P. K. Sahu, R. Kharel, S. Shome, S. Goswami, S. Konar, *Coord. Chem. Rev.* **2023**, *475*, 214871; h) J. Cirera, E. Ruiz, S. Alvarez, F. Neese, J. Kortus, *Chem. Eur. J.* **2009**, *15*, 4078; i) O. Waldmann, *Inorg. Chem.* **2007**, *46*, 10035.

[4] a) M. Cirulli, E. Salvadori, Z.-H. Zhang, M. Dommett, F. Tuna, H. Bamberger, J. E. M. Lewis, A. Kaur, G. J. Tizzard, J. V. Slageren, R. Crespo-Otero, S. M. Goldup, M. M. Roessler, *Angew. Chem. Int. Ed.* **2021**, *60*, 16051; b) A. K. Mondal, J. Jover, E. Ruiz, S. Konar, *Dalton Trans.* **2019**, *48*, 25; c) S. K. Gupta, S. V. Rao, S. Demeshko, S. Dechert, E. Bill, M. Atanasov, F. Neese, F. Meyer, *Chem. Sci.* **2023**, *14*, 6355.

[5] a) M. A. Palacios, I. F. Díaz-Ortega, H. Nojiri, E. A. Suturina, M. Ozerov, J. Krzystek, E. Colacio, *Inorg. Chem. Front.* **2020**, *7*, 4611; b) B. Cahier, M. Perfetti, G. Zakhia, D. Naoufal, F. El-Khatib, R. Guillot, E. Rivière, R. Sessoli, A.-L. Barra, N. Guihéry, T. Mallah, *Chem. Eur. J.* **2017**, *23*, 3648; c) A. Świtlicka, B. Machura, J. n Cano, F. Lloret, M. Julve, *ChemistrySelect* **2021**, *6*, 576; d) S. K. Gupta, H. H. Nielsen, A. M. Thiel, E. A. Klahn, E. Feng, H. B. Cao, T. C. Hansen, E. L. Berna, A. Gukasov, I. Kibalin, S. Dechert, S. Demeshko, J. Overgaard, F. Meyer, *JACS Au* **2023**, *3*, 429; e) A. Sarkar, S. Dey, G. Rajaraman, *Chem. Eur. J.* **2020**, *26*, 14036; f) A. K. Mondal, M. Sundararajan, S. Konar, *Dalton Trans.* **2018**, *47*, 3745; g) M. Wang, H. J. Xu, T. M. Sun, H. H. Cui, Y.-Q. Zhang, L. Chen, Y. F. Tang, *J. Solid State Chem.* **2021**, *299*, 122209; h) H. H. Cui, F. Lu, X. T. Chen, Y. Q. Zhang, W. Tong, Z. L. Xue, *Inorg. Chem.* **2019**, *58*, 12555; i) A. Raza, M. Perfetti *Coord. Chem. Rev.* **2023**, *490*, 215213; j) Y. Peng, T. Bodenstein, K. Fink, V. Mereacre, C. E. Anson, A. K. Powell, *Phys. Chem. Chem. Phys.* **2016**, *18*, 30135; k) W. Lv, H. H. Cui, L. Chen, Y. Q. Zhang, X. T. Chen, Z. Wang, Z.-W. Ouyang, Z. L. Xue, *Dalton Trans.* **2022**, *51*, 7530; l) Y.-Z. Zhang, S. Gómez-Coca, A. J. Brown, M. R. Saber, X. Zhang, K. R. Dunbar, *Chem. Sci.* **2016**, *7*, 6519; m) T. J. Woods, M. F. Ballesteros-Rivas, S. Gómez-Coca, E. Ruiz, K. R. Dunbar, *J. Am. Chem. Soc.* **2016**, *138*, 16407.

[6] a) N. Ishikawa, M. Sugita, T. Ishikawa, S.-Y. Koshihara, Y. Kaizu, *J. Am. Chem. Soc.* **2003**, *125*, 8694; b) Y. C. Chen, J. L. Liu, L. Ungur, J. Liu, Q. W. Li, L. F. Wang, Z. P. Ni, L. F. Chibotaru, X. M. Chen, M. L. Tong, *J. Am. Chem. Soc.* **2016**, *138*, 2829; c) J. Liu, Y. C. Chen, J. L. Liu, V. Vieru, L. Ungur, J. H. Jia, L. F. Chibotaru, Y. Lan, W. Wernsdorfer, S. Gao, X. M. Chen, M. L. Tong, *J. Am. Chem. Soc.* **2016**, *138*, 5441; d) S. K. Gupta, T. Rajeshkumar, G. Rajaraman, R. Murugavel, *Chem. Sci.* **2016**, *7*, 5181; e) S. D. Jiang, B. W. Wang, H. L. Sun, Z. M. Wang, S. Gao, *J. Am. Chem. Soc.* **2011**, *133*, 4730; f) L. Ungur, J. J. Le Roy, I. Korobkov, M. Murugesu, L. F. Chibotaru, *Angew. Chem. Int. Ed.* **2014**, *53*, 4413; g) C. A. P. Goodwin, F. Ortu, D. Reta, N. F. Chilton, D. P. Mills, *Nature* **2017**, *548*, 439; h) P. Zhang, L. Zhang, C. Wang, S. Xue, S.-Y. Lin, J. Tang, *J. Am. Chem. Soc.* **2014**, *136*, 4484; i) F.-S. Guo, B. M. Day, Y.-C. Chen, M.-L. Tong, A. Mansikkamäki, R. A. Layfield, *Science* **2018**, *362*, 1400; j) J. L. Liu, Y. C. Chen, M. L. Tong, *Chem. Soc. Rev.* **2018**, *47*, 2431; k) J. Wang, C. Y. Sun, Q. Zheng, D. Q. Wang, Y. T. Chen, J. F. Ju, T. M. Sun, Y. Cui, Y. Ding, Y. F. Tang, *Chem. Asian J.* **2023**, *18*, e202201297; l) S. K. Kushvaha, P. Ravichandran, C. Dan, L. Ungur, N. Suryadevara, M. Ruben, K. C. Mondal, *Eur. J. Inorg. Chem.* **2024**, *27*, e202300598.

[7] a) P. S. Perlepe, D. Maniaki, E. Pilichos, E. Katsoulakou, S. P. Perlepes, *Inorganics* **2020**, *8*, 39; b) A. R. -Diéguez, S. P. Yáñez, L. R. Rubio, J. M. Seco, J. Cepeda, *CrystEngComm* **2017**,*19*, 2229; c) R. Boča, C. Rajnák, *Coord. Chem. Rev.* **2021**, *430*, 213657; d) A. K. Bar, C. Pichon, N. Gogoi, C. Duhayon, S. Ramasesha, J. P. Sutter, *Chem. Commun.* **2015**, *51*, 3616; e) M. A. Zykin, P. l. E. Kazin, M. Jansen, *Chem. Eur. J.* **2020**, *26*, 8834; f) M. Wakizaka, R. Ishikawa, H. Tanaka, S. Gupta, S. Takaishi, M. Yamashita, *Small* **2023**, *19*, 2301966; g) K. Diller, A. Singha, M. Pivetta, C. Wackerlin, R. Hellwig, A. Verdini, A. Cossaro, L. Floreano, E. Velez-Fort, J. Dreiser, S. Rusponi, H. Brune, *RSC Adv.* **2019**, *9*, 34421; h) I. Nemec, R. Herchel, Z. Travnicek, *Dalton Trans.* **2016**, *45*, 12479; i) Ivan Nemec, R. Marx, R. Herchel, P. Neugebauer, J. V. Slageren, Z. Travnicek, *Dalton Trans.* **2015**, *44*, 15014.

[8] a) X. N. Yao, J. Z. Du, Y. Q. Zhang, X. B. Leng, M. W. Yang, S. D. Jiang, Z. X. Wang, Z. W. Ouyang, L. Deng, B. W. Wang, S. Gao, *J. Am. Chem. Soc.* **2017**, *139*, 373; b) P. C. Bunting, M. Atanasov, E. Damgaard-Møller, M. Perfetti, I. Crassee, M. Orlita, J. Overgaard, J. V. Slageren, *Science* **2018**, *362*, eaat7319; c) E. Carl, S. Demeshko, F. Meyer, D. Stalke, *Chem. Eur. J.* **2015**, *21*, 10109; d) C. M. Legendre, E. Damgaard-Møller, J. Overgaard, D. Stalke, *Eur. J. Inorg. Chem.* **2021**, *2021*, 3108; e) Y. Rechkemmer, F. D. Breitgoff, M. van der Meer, M. Atanasov, M. Hakl, M. Orlita, P. Neugebauer, F. Neese, B. Sarkar, J. V. Slageren, *Nat. Commun.* **2016**, *7*, 10467; f) X. N. Yao, M. W. Yang, J. Xiong, J. J. Liu, C. Gao, Y. S. Meng, S. D. Jiang, B. W. Wang, S. Gao, *Inorg. Chem. Front.* **2017**, *4*, 701; g) J. Vallejo, E. Pardo, M. Viciano-Chumillas, I. Castro, P. Amor'os, M. Deniz, C. Ruiz-Perez, C. Yuste-Vivas, J. Krzystek, M. Julve, F. Lloret, J. Cano, *Chem. Sci.* **2017**, *8*, 3694; h) C. Rajnak, J. Titis, O. Fuhr, M. Ruben, R. Boca, *Inorg. Chem.* **2014**, *53*, 8200; i) P. Kumar, D. J. Santa Lucia, K. Kaniewska-Laskowska, S. V. Lindeman, A. Ozarowski, J. Krzystek, M. Ozerov, J. Telser, J. F. Berry, A. T. Fiedler, *Inorg. Chem.* **2020**, *59*, 16178; j) M. R. Saber, M. K. Singh, K. R. Dunbar, *Chem. Commun.* **2020**, *56*, 8492; k) A. A. Pavlov, D. Y. Aleshin, S. A. Savkina, A. S. Belov, N. N. Efimov, J. Nehrkorn, M. Ozerov, Y. Z. Voloshin, Y. V. Nelyubina, V. V. Novikov, *ChemPhysChem* **2019**, *20*, 1001; l) A. Landart-Gereka, M. M. Quesada-Moreno, I. F. Dıaz-Ortega, H. Nojiri, M. Ozerov, J. Krzystek, M. A. Palacios, E. Colacio, *Inorg. Chem. Front.* **2022**, *9*, 2810; m) P. K. Sahu, A. Mondal, S. Konar, *Dalton*

Trans. **2021**, *50*, 3825; n) L. Rigamonti, N. Bridonneau, G. Poneti, L. Tesi, L. Sorace, D. Pinkowicz, J. Jover, E. Ruiz, R. Sessoli, A. Cornia, *Chem. Eur. J.* **2018**, *24*, 8857; o) A. K. Mondal, J. Jover, E. Ruiz, S. Konar, *Chem. Eur. J.* **2017**, *23*, 12550; p) Y. Cui, Y. Xu, X. Liu, Y. Li, B. L. Wang, Y. Dong, W. Li, S. Lei, *Chem. Asian J.* **2019**, *14*, 2620.

[9] a) I. Nemec, R. Herchel, Z. Trávníček, *Sci. Rep.* **2015**, *5*, 10761; b) J. N. Giraldo, J. Hrubý, S. Vavrečková, O. F. Fellner, L. Havlicek, D. Henry, S. de Silva, R. Herchel, M. Bartoš, I. Salitros, V. T. Santana, P. Barbara, I. Nemec, Petr Neugebauer, *Phys. Chem. Chem. Phys.* **2023**, *25*, 29516.

[10] a) S. Alvarez, P. Alemany, D. Casanova, J. Cirera, M. Llunell, D. Avnir, *Coord. Chem. Rev.* **2005**, *249*, 1693; b) P. Debye, *Ann. Phys.* **1912**, *344*, 789; c) J. Cirera, E. Ruiz, S. Alvarez, *Chem. Eur. J.* **2006**, *12*, 3162.

[11] R. F. W. Bader, *Atoms in Molecules*, Oxford University Press, **1994**.

[12] T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580.

[13] T. Lu, F. Chen, *J. Mol. Graphics Modell.* **2012**, *38*, 314.

[14] AIMAll (Version 19.10.12), Todd A. Keith, TK Gristmill Software, Overland Park KS, USA, **2019** (aim.tkgristmill.com).

[15] F. Neese, *WIREs Comput. Mol. Sci.* **2018**, *8*, e1327.

[16] a) D. Jayatilaka, B. Dittrich, *Acta Crystallogr. Sect. A.* **2008**, *64*, 383; b) S. C. Capelli, H.-B. Bürgi, B. Dittrich, S. Grabowsky, D. Jayatilaka, *IUCrJ* **2014**, *1*, 361.

[17] F. Kleemiss, O. V. Dolomanov, M. Bodensteiner, N. Peyerimhoff, L. Midgley, L. J. Bourhis, A. Genoni, L. A. Malaspina, D. Jayatilaka, J. L. Spencer, F. White, B. Grundkötter-Stock, S. Steinhauer, D. Lentz, H. Puschmann, S. Grabowsky, *Chem. Sci.* **2021**, *12*, 1675.

[18] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339.

[19] E. Espinosa, E. Molins, C. Lecomte, *Chem. Phys. Lett.* **1998**, *285*, 170.

[20] J. Jurakova, I. Salitros, *Monatsh. Chem.* **2022**, *153*, 1001.

[21] a) F. E. Mabbs, D. J. Machin, *Magnetism and Transition Metal Complexes* Dover Publications: Mineola, NY, **2008**; b) I. Nemec, R. Herchel, M. Kern, P. Neugebauer, J. V. Slageren, Z. Travnicek, *Materials* **2017**, *10*, 249.

[22] M. I Atanasov, D. Aravena, E. Suturina, E. Bill, D. Maganas, F. Neese, *Coord. Chem. Rev.* **2015**, *289–290*, 177.

[23] F. Neese, *J. Chem. Phys.* **2005**, *122*, 034107.

[24] a) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297; b) F. Weigend, *Phys. Chem. Chem. Phys.* **2002**, *4*, 4285.

[25] F. Neese, F. Wennmohs, A. Hansen, U. Becker, *Chem. Phys.* **2009**, *356*, 98.

[26] I. Nemec, O. F. Fellner, B. Indruchova, R. Herchel, *Materials* **2022**, *15*, 1064.

[27] a) C. M. Wu, J. En Tsai, G. H. Lee, E. C. Yang, *Dalton Trans.* **2020**, *49*, 16813; b) J. M. Zadrozny, J. Telser, J. R. Long, *Polyhedron* **2013**, *64*, 209; c) R. Mitsuhashi, S. Hosoya, T. Suzuki, Y. Sunatsuki, H. Sakiyama, M. Mikuriya, *Dalton Trans.* **2019**, *48*, 395; d) D. Tu, D. Shao, H. Yan, C. Lu, *Chem. Commun.* **2016**, *52*, 14326; e) M. Böhme, S. Ziegenbalg, A. Aliabadi, A. Schnegg, H. Görlsa, W. Plass, *Dalton Trans.* **2018**, *47*, 10861.

[28] a) M. E. Boulon, G. Cucinotta, J. Luzon, C. Degl'Innocenti, M. Perfetti, K. Bernot, G. Calvez, A. Caneschi, R. Sessoli, *Angew. Chem. Int. Ed.* **2013**, *52*, 350; b) H. A. Kramers, *Proc. R. Acad. Sci. Amsterdam* **1930**, *33*, 959; c) A. L. Barra, A. Caneschi, A. Cornia, D. Gatteschi, L. Gorini, L. P. Heiniger, R. Sessoli, L. Sorace, *J. Am. Chem. Soc.* **2007**, *129*, 10754.

[29] a) K. N. Shrivastava, *Phys. Status Solidi B* **1983**, *117*, 437; b) A. Singh, K. N. Shrivastava, *Phys. Status Solidi B* **1979**, *95*, 273.

[30] a) K. S. Cole, R. H. Cole, *J. Chem. Phys.* **1941**, *9*, 341.