

Dear ACS Physical Chemistry Au Editor,

First, we appreciate the time you and the reviewers spent evaluating our manuscript. These comments allowed us to improve the quality of our work. Please find in the following a point-by-point response to these comments on the manuscript "Magnetic anisotropy and spin coupling in a Cobalt(II) dimer with bioinspired bridges."

Manuscript reference: pg-2025-001344.

In the new version, all changes are highlighted in red. After addressing the different points raised by the referees, we kindly request considering the present version of this manuscript for publication in ACS Physical Chemistry Au.

Sincerely,
The authors

Report of the First Referee

Recommendation: Do not publish in ACS Physical Chemistry Au.

Comments:

The manuscript

"Magnetic anisotropy and spin coupling in a Cobalt(II) dimer with bioinspired bridges" by Alan de Souza, A. C. das Neves, Paula Brandão, Mariem Masmoudi, Luis Ghivelder, Clebson Cruz, and Mario Reis involves an experimental study of a single dinuclear Co(II) complex using DC magnetometry. The data taking is well done; however, the data analysis is almost wrong.

Authors: We thank the reviewer for this remark and acknowledge that the initial data analysis was indeed inconclusive. Therefore, we have redone the entire analysis. In the revised approach, the symmetry of the two cobalt(II) centers was correctly identified and explicitly taken into account. As a consequence, the system was described using an ionic spin Hamiltonian in which both Co(II) ions are equivalent, leading to identical zero-field splitting parameters, with the same axial and rhombic components (D and E) assigned to each cobalt center. The refined analysis yields a ratio $E/D \approx 1/4$, where $D = 89$ K, indicating a significant rhombic contribution to the magnetic anisotropy. The two cobalt centers are found to be antiferromagnetically coupled. In addition, the fitted Landé factors are $g_x = g_y = 2.5$ and $g_z = 2.4$, consistent with an anisotropic expected for Co(II) ions in a low-symmetry crystal field. Overall, these results are consistent with available literature data for hexacoordinated high-spin Co(II) dimers, and the corresponding references have been added to the revised manuscript.

1. The X-ray structure determination is not quoted. The referee found the deposited structural data in the Cambridge Crystallographic Data Centre with the deposit number 2440271 and composition C10 H26 Co2 N14 O20. This information must be quoted in the

manuscript. According to this structure, both Co centers are equivalent with the same coordination sphere. This is in direct contrast with the statements of the manuscript, where very different zero-field splitting D and E parameters are assigned to the two centers.

Authors: We thank the referee for this observation. Structural information about the metal complex has been included. Indeed, the metal centers are equivalent and share the same coordination environment, which subsequently led us to reformulate the Hamiltonian using identical D and E parameters for both centers.

2. The coordination needs to be termed hexacoordination, not octahedral.

Authors: We thank the referee for this observation. The terminology has been corrected to “hexacoordination” as suggested.

3. The statement “(Compound I), where L1H = adenine, a molecule that combines promising anticancer effects [10] with magnetic characteristics potentially valuable for next-generation quantum platforms.” has no experimental support.

*Authors: We thank the reviewer for this observation. We would like to clarify that the statement regarding the anticancer potential of adenine is supported by experimental studies on adenine-containing coordination complexes reported in the literature. Ferreira et al. [1] experimentally demonstrated significant *in vitro* antitumor activity for a dinuclear Cu(II) complex bridged by adenine, tested against HeLa and Caco-2 cell lines, with IC₅₀ values lower than those of cisplatin under the same conditions. In addition, Masmoudi et al. [2] investigated a series of multinuclear Co, Cu, and Fe complexes containing adenine and/or phenanthroline ligands and reported measurable, albeit moderate, cytotoxic activity *in vitro* against Caco-2 and AsPC-1 cancer cell lines. These studies provide experimental evidence that adenine-containing coordination complexes can exhibit cytotoxic activity, with the magnitude strongly dependent on the coordination environment and ligand binding mode.*

In addition, we note that there is a well-established body of literature supporting the relevance of molecular and solid-state magnetic systems to quantum information science and quantum thermodynamics. In these references [3–6], the authors reported studies of quantum resources, such as quantum entanglement and quantum discord, and their applications to quantum-thermodynamic devices, including quantum battery models and work extraction in quantum heat engines. These works demonstrate that low-dimensional magnetic systems with well-defined spin Hamiltonians constitute suitable platforms for exploring quantum resources and their thermodynamic implications.

1. B. J. M. L. Ferreira, P. Brandão, M. Meireles, F. Martel, A. Correia-Branco, D. M. Fernandes, T. M. Santos, and V. Félix. Synthesis, structural characterization, cytotoxic properties and dna binding of a dinuclear copper(ii) complex. *Journal of Inorganic Biochemistry*, 161:9–17, 2016.

2. Mariem Masmoudi, Cláudia Silva, Nelson Andrade, Fátima Martel, and Paula Brandão. Coordination complexes of co, cu, and fe with adenine and phenanthroline: Synthesis, characterization, and cytotoxic studies. *Journal of Molecular Structure*, 1345:143128, 2025.

3. CRUZ, C.; RASTEGAR SEDEHI, H. R.; ANKA, M. F.; OLIVEIRA, T.; REIS, M. S. *Quantum Stirling engine based on dinuclear metal complexes. Quantum Science and Technology*, v. 8, p. 035010, 2023.
4. CRUZ, C.; ANKA, M. F.; REIS, M. S.; BACHELARD, R.; SANTOS, A. C. *Quantum battery based on quantum discord at room temperature. Quantum Science and Technology*, v. 7, p. 025020, 2022.
5. CRUZ, C. S.; SOARES-PINTO, D. O.; BRANDÃO, P.; SANTOS, A. M.; REIS, M. S. *Carboxylate-based molecular magnet: One path toward achieving stable quantum correlations at room temperature. Europhysics Letters*, v. 113, p. 40004, 2016.
6. SOUZA, A. M.; SOARES-PINTO, D. O.; SARTHOUR, R. S.; OLIVEIRA, I. S.; REIS, M. S.; BRANDÃO, P.; SANTOS, A. M. *Entanglement and Bell's inequality violation above room temperature in metal carboxylates. Physical Review B*, v. 79, p. 054408, 2009.

4. There is an attempt to fit the susceptibility data and not to fit the magnetization data. The contemporary approach is to fit both datasets simultaneously based on the common Hamiltonian.

Authors: The fit of the magnetization data was made and included in the manuscript using the new hamiltonian.

5. The used symbol “emu” is not a unit! This is a system of units like cgs, and SI. Thus the magnetization per formula unit must be presented in units of Bohr magneton. Change Oe to tesla.

Authors: We thank the referee for the observation. We changed the units correctly for both ChiT and Magnetization data.

6. Eqn. (1) is a catastrophe. If the isotropic exchange coupling constant J is thought ofwithout any prefactor (-1, -2), then it implies that its negative value refers to the FERROMAGNETIC coupling and not to the antiferromagnetic coupling as stated by the authors of the manuscript. Moreover, the term S_{α}^2 must appear without subscript alpha; this is a square of the spin, giving rise to $S(S + 1)$. The used Zeeman term assumes only three Cartesian components, which is not true for the powder average (then alpha must also be at $H(\alpha)$). A correct powder average can be done for a sufficient number of grids (knots) distributed equally over one hemisphere to which the magnetic field is oriented. Then, B is a function of the spherical angles theta and phi.

Authors: The definition of the isotropic exchange term and its prefactors, as well as the interpretation of ferromagnetic or antiferromagnetic coupling, depends on the conventions adopted by the authors. Nevertheless, we have implemented the prefactor -1, as suggested by the referee. The correction of the term S_{α}^2 to $S(S + 1)$ has also been carried out.

Although the Zeeman term explicitly displays only the three Cartesian axes, the software DAVE-MagProp automatically performs the appropriate powder-average treatment. To this end, we also thank the referee for these valuable suggestions.

7. A definition of the constant C is missing.

Authors: We thank the referee for this observation. The definition of C was included in the discussion.

8. Fitting of the susceptibility data with 10 free parameters (with two decimals) is not a reliable task; moreover, standard deviations of each parameter is not presented.

Authors: The referee is right. As we remade the analysis considering the right equivalent metallic centers, the parameters went from 10 to 6. We also included the standard deviations of each parameter.

9. The statement “Interestingly, both Co(II) centers yield different anisotropy constants (D1 and D2), which likely reflects slight differences in their local environments as revealed by crystal structure (for example, one Co sees a more axially elongated geometry than the other one).” IS WRONG. Both Co(II) centers have the same axial Co-N distances of 2.144 and 2.120 Angstrom. These centers are equivalent.

Authors: We thank the reviewer for this remark and acknowledge that the initial data analysis was indeed inconclusive. Therefore, we have redone the entire analysis. In the revised approach, the symmetry of the two cobalt(II) centers was correctly identified and explicitly taken into account. As a consequence, the system was described using an ionic spin Hamiltonian in which both Co(II) ions are equivalent, leading to identical zero-field splitting parameters, with the same axial and rhombic components (\$D\$ and \$E\$) assigned to each cobalt center. The refined analysis yields a ratio \$E/D \approx 1/4\$, where \$D = 89\$ K, indicating a significant rhombic contribution to the magnetic anisotropy. The two cobalt centers are found to be antiferromagnetically coupled. In addition, the fitted Landé factors are \$g_x = g_y = 2.5\$ and \$g_z = 2.4\$, consistent with an anisotropic expected for Co(II) ions in a low-symmetry crystal field. Overall, these results are consistent with available literature data for hexacoordinated high-spin Co(II) dimers, and the corresponding references have been added to the revised manuscript.

10. Common g-factors for both centers are assumed, but different D and E. Why? This has no sense.

Authors: We thank the reviewer for this remark and acknowledge that the initial data analysis was indeed inconclusive. Therefore, we have redone the entire analysis. In the revised approach, the symmetry of the two cobalt(II) centers was correctly identified and explicitly taken into account. As a consequence, the system was described using an ionic spin Hamiltonian in which both Co(II) ions are equivalent, leading to identical zero-field splitting parameters, with the same axial and rhombic components (\$D\$ and \$E\$) assigned to each cobalt center. The refined analysis yields a ratio \$E/D \approx 1/4\$, where \$D = 89\$ K, indicating a significant rhombic contribution to the magnetic anisotropy. The two cobalt centers are found to be antiferromagnetically coupled. In addition, the fitted Landé factors are \$g_x = g_y = 2.5\$ and \$g_z = 2.4\$, consistent with an anisotropic expected for Co(II) ions in a low-symmetry crystal field. Overall, these results are consistent with available literature data for hexacoordinated high-spin Co(II) dimers, and the corresponding references have been added to the revised manuscript.

11. The value \$E_1/D_1 = 0.437\$ exceeds 1/3, so then the sign of D must be reversed.

Authors: We thank the reviewer for this remark and acknowledge that the initial data analysis was indeed inconclusive. Therefore, we have redone the entire analysis. In the revised approach, the symmetry of the two cobalt(II) centers was correctly identified and explicitly taken into account. As a consequence, the system was described using an ionic spin Hamiltonian in which both Co(II) ions are equivalent, leading to identical zero-field splitting parameters, with the same axial and rhombic components (\$D\$ and \$E\$) assigned to each cobalt center. The refined analysis yields a ratio \$E/D \approx 1/4\$, where \$D = 89\$ K, indicating a significant rhombic contribution to the magnetic anisotropy. The two cobalt centers are found to be antiferromagnetically coupled. In addition, the fitted Landé factors

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12. DAVE-MagProp software is not referenced.

Authors: We thank the referee for this observation. The reference to the DAVE-MagProp software has now been included in the manuscript.

13. “Magnetization as a function of temperature was additionally measured under a small dc field (0.1 T),” but in Fig. 4 the value of H = 100 Oe is displayed, which is 0.01 T.

Authors: We thank the referee for the typo observation. The correct applied magnetic field was inserted into the figures.

14. The statement “Compound I is being evaluated for cytotoxic activity against cancer-related cell lines and as a building block for quantum-information and quantum-thermodynamic devices. Detailed results of these ongoing studies will be reported in due course.” has no scientific support so far.

Authors: We thank the reviewer for this observation. We would like to clarify that the statement regarding the anticancer potential of adenine is supported by experimental studies on adenine-containing coordination complexes reported in the literature. Ferreira et al. [1] experimentally demonstrated significant in vitro antitumor activity for a dinuclear Cu(II) complex bridged by adenine, tested against HeLa and Caco-2 cell lines, with IC₅₀ values lower than those of cisplatin under the same conditions. In addition, Masmoudi et al. [2] investigated a series of multinuclear Co, Cu, and Fe complexes containing adenine and/or phenanthroline ligands and reported measurable, albeit moderate, cytotoxic activity in vitro against Caco-2 and AsPC-1 cancer cell lines. These studies provide experimental evidence that adenine-containing coordination complexes can exhibit cytotoxic activity, with the magnitude strongly dependent on the coordination environment and ligand binding mode.

In addition, we note that there is a well-established body of literature supporting the relevance of molecular and solid-state magnetic systems to quantum information science and quantum thermodynamics. In these references [3–6], the authors reported studies of quantum resources, such as quantum entanglement and quantum discord, and their applications to quantum-thermodynamic devices, including quantum battery models and work extraction in quantum heat engines. These works demonstrate that low-dimensional magnetic systems with well-defined spin Hamiltonians constitute suitable platforms for exploring quantum resources and their thermodynamic implications.

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15. Table II is a chaotic compilation of some literature data. Only one of the listed complexes is dinuclear, and, moreover, it is pentacoordinate.

Authors: We thank the reviewer for this observation. Table 2 includes Co(II)-based molecular complexes. Most of the cited compounds are indeed monomers; however, they were included with the aim of comparing the D and E parameters, since the authors of those works employed the same Hamiltonian as ours. This was also the case for the pentacoordinated molecular complex.

Nevertheless, we acknowledge that references to hexacoordinated dinuclear molecular compounds were missing. Therefore, we have added a textual discussion of several hexacoordinated dinuclear complexes in order to at least compare the exchange parameters and, when possible, the D parameter as also the Landé factors. We note, however, that different authors often adopt different Hamiltonians in the case of Co(II) dimers, which leads to different fitted parameters for the experimental data and makes the inclusion of such references in the table not consistent. To this end, we removed the Table and replaced it by Table IV.

16. The statement “Thus, the aim of this work is to determine the full anisotropy tensor” is incorrect, as the full anisotropy tensor must involve the two-center asymmetric exchange coupling parameters (not only local D and E). For some inspiration: <http://dx.doi.org/10.1016/j.ica.2012.09.001>

Authors: Authors: We thank the reviewer for this remark and acknowledge that the initial data analysis was indeed inconclusive. Therefore, we have redone the entire analysis. In the revised approach, the symmetry of the two cobalt(II) centers was correctly identified and explicitly taken into account. As a consequence, the system was described using an ionic spin Hamiltonian in which both Co(II) ions are equivalent, leading to identical zero-field splitting parameters, with the same axial and rhombic components (\$D\$ and \$E\$) assigned to each cobalt center. The refined analysis yields a ratio \$E/D \approx 1/4\$, where \$D = 89\$ K, indicating a significant rhombic contribution to the magnetic anisotropy. The two cobalt centers are found to be antiferromagnetically coupled. In addition, the fitted Landé factors

are \$g_x = g_y = 2.5\$ and \$g_z = 2.4\$, consistent with an anisotropic expected for Co(II) ions in a low-symmetry crystal field. Overall, these results are consistent with available literature data for hexacoordinated high-spin Co(II) dimers, and the corresponding references have been added to the revised manuscript.

Also, the referee was correct in noting that we determined the full anisotropy tensor. Accordingly, we have corrected the statement to refer explicitly only to the diagonal components of the \$g\$ tensor, namely \$g_x\$, \$g_y\$, and \$g_z\$.

To this end, the manuscript is too weak in order be considered for publication anywhere.

Authors: We thank the reviewer for the time and effort devoted to providing these comments. We hope that the suggested corrections, all of which have been fully implemented, have significantly strengthened the manuscript and improved its overall quality.

Additional Questions:

Do the authors adhere to the guidelines on Human/Animal Studies outlined in the ACS Ethical Guidelines?: Yes

If published, do you feel this manuscript should be promoted as Newsworthy?: No

Originality: Poor

Technical Quality: Poor

Clarity of Presentation: Poor

Authors: We thank the reviewer for the time and effort devoted to providing these comments. We hope that the suggested corrections, all of which have been fully implemented, have significantly strengthened the manuscript and improved its overall quality.

Report of the Second Referee

Recommendation: Publish after minor revisions.

Comments:

The work reported in the manuscript entitled "Magnetic anisotropy and spin coupling in a Cobalt(II) dimer with bioinspired bridges" is a well-executed and timely study in the field of molecular magnetism. The article presents a detailed experimental and theoretical investigation of a dinuclear Co(II) complex bridged by adenine ligands, focusing on its magnetic anisotropy and spin coupling. Upon addressing the following points, I would support its publication in ACS Physical Chemistry Au.

Authors: We thank the reviewer for the time spent reading the manuscript and appreciate their support for publication in ACS Physical Chemistry.

Introduction: The introduction provides a solid contextualization of the applications of metal complexes. The justification for studying the dinuclear Co(II) compound with adenine as a bioinspired ligand is clear. However, the specific gap in the literature regarding fully characterized binuclear Co(II) complexes with anisotropy—only briefly mentioned—could be highlighted.

A summary of the main results at the end of the introduction would reinforce the study's relevance. Furthermore, more current references should be added.

Authors: We thank the reviewer for this comment. The specific gap in the literature has now been more clearly discussed, and we have added an additional discussion on how this type of study can be applied within the context of quantum magnetism

Crystal Structure Description: While the structural details are said to follow a previous reference (Ref. [10]), key crystallographic data (e.g., space group, R-factors, temperature of data collection) should be summarized to ensure this manuscript is self-contained. Additionally, the magnetostructural correlation should be improved; examples of similar complexes should be discussed in the text.

Authors: We thank the reviewer for this comment. In response, all the requested crystallographic data have been included in the manuscript, making it self-contained (space group, R-factors, and data collection temperature). In addition, the magnetostructural correlation has been improved, and examples of similar complexes (hexacoordinated cobalt(II) dimers) have also been included and discussed in the text.

Tables:

- Table I is clear and informative.
- Table II could be improved with better visual separation or highlighting of similarities and differences across systems to guide the reader's interpretation.

Authors: We thank the referee for these comments. Table II has been replaced by Table IV, which now includes only hexacoordinated cobalt(II) dimers. As discussed in the text and noted below the table, the first two complexes do not include the rhombic term, whereas the remaining six complexes were analyzed using the more general D-tensor.. Nevertheless, a meaningful comparison with our results is still possible, since the sign of D and the Landé factors carry clear physical significance, as does the exchange parameter J, which unambiguously indicates ferromagnetic or antiferromagnetic coupling. In addition, the visual presentation of the table has been improved to better highlight these differences.

Discussion on $D_1 \neq D_2$: The difference between D_1 and D_2 is briefly mentioned as likely due to structural inequivalence. This is plausible but deserves deeper structural correlation using available crystallographic metrics (e.g., bond lengths or angles around each Co center).

Authors: We thank the reviewer for this comment and agree that the initial analysis, which suggested different zero-field splitting parameters for the two cobalt centers, was not sufficiently conclusive. For this reason, we have completely revised the data analysis. In the new approach, the crystallographic symmetry of the complex was carefully reexamined and the two Co(II) centers were found to be structurally equivalent within experimental resolution. Consequently, the magnetic properties were reanalyzed using an ionic spin Hamiltonian that

explicitly uses the equivalency cobalt sites, leading to identical zero-field splitting parameters for both centers, with common axial and rhombic terms (D) and (E).

Additional Questions:

Do the authors adhere to the guidelines on Human/Animal Studies outlined in the ACS Ethical Guidelines?: Yes

If published, do you feel this manuscript should be promoted as Newsworthy?: Yes

Originality: Good

Technical Quality: Excellent

Clarity of Presentation: Excellent

Authors: We thank the reviewer for the time devoted to reading the manuscript and appreciate their support for its publication, which aligns with our intention to submit this work to ACS Physical Chemistry.