

Ammonia Binding

Vapochromism and Magnetochemical Switching of a Nickel(II) Paddlewheel Complex by Reversible NH₃ Uptake and Release

Katharina M. Fürpaß, Lydia M. Peschel, Jörg A. Schachner, Sergey M. Borisov, Heinz Krenn, Ferdinand Belaj, and Nadia C. Mösch-Zanetti*

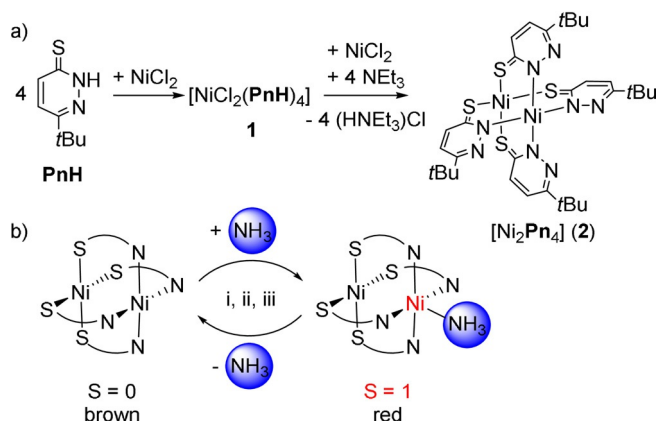
Abstract: Reaction of [NiCl₂(PnH)₄] (**1**) (PnH = 6-*tert*-butylpyridazine-3-thione) with NiCl₂ affords the binuclear paddlewheel (PW) complex [Ni₂(Pn)₄] (**2**). Diamagnetic complex **2** is the first example of a PW complex capable of reversibly binding and releasing NH₃. The NH₃ ligand in [Ni₂(Pn)₄·NH₃] (**2**·NH₃) enforces major spectroscopic and magnetic susceptibility changes, thus displaying vapochromic properties ($\lambda_{\max}(\mathbf{2}) = 532 \text{ nm}$, $\lambda_{\max}(\mathbf{2}\cdot\text{NH}_3) = 518 \text{ nm}$) and magnetochemical switching (**2**: $S = 0$; **2**·NH₃: $S = 1$). Upon repeated adsorption/desorption cycles of NH₃ the PW core remains intact. Compound **2** can be embedded into thin polyurethane films (**2**^P) under retention of its sensing abilities. Therefore, **2** qualifies as reversible optical probe for ammonia. The magnetochemical switching of **2** and **2**·NH₃ was studied in detail by SQUID measurements showing that in **2**·NH₃, solely the Ni atom coordinated the NH₃ molecule is responsible for the paramagnetic behavior.

Introduction

The paddlewheel (PW) motif with four bridging ligands spanning two metal centers of the general formula [M₂(XY)₄] (X,Y=O, N, P, S, C) is among the most studied metal connectors in coordination chemistry.^[1] Recently, we have begun to study the relatively unexplored chemistry of the *S,N*-bidentate ligand 6-*tert*-butyl-pyridazine-3-thione (PnH).^[2] Comparatively few structurally characterized divalent group

How to cite: *Angew. Chem. Int. Ed.* **2021**, *60*, 13401–13404
International Edition: doi.org/10.1002/anie.202102149
German Edition: doi.org/10.1002/ange.202102149

10 PWs have been published (Pt ≈ 100, Pd, Ni < 15 each). Reported Ni₂-PWs are either symmetrically bridged by *O,O*-,^[3] *S,S*-,^[4,5] or *N,N*-^[6–9] type ligands or asymmetrically bridged by *S,O*-^[10] or *S,N*-bridging ligands (Scheme 1).^[11,12] In principle four different isomers are possible for an asymmetric ligand system like PnH (Figure S4).



Scheme 1. a) Stepwise synthesis of [Ni₂(Pn)₄] (**2**) via complex **1**. b) Illustration of reversible NH₃ coordination triggering spin-state switching and vapochromism via three different pathways: i) dissolved **2** + NH₃(aq.) ↔ **2**·NH₃, 0.01 mbar, 110°C, 1 h. ii) solid **2** + NH₃(g) ↔ **2**·NH₃, 0.01 mbar, 110°C, 1 h. iii) encapsulated **2**^P + NH₃(g) ↔ **2**^P·NH₃, 20 min soak in H₂O.

The remarkable magnetic properties of PW complexes have been previously described in literature. If metal-metal bonds are absent, divalent group 10 PWs are expected to be diamagnetic because of the square-planar ligand field around the two metal sites.^[13] Pd^{II} and Pt^{II} PWs have been shown to strictly maintain their essentially square-planar geometry around the metal centers. Ni₂-PWs on the other hand have been reported to be mainly paramagnetic (some exceptions are known^[5]), because of additionally coordinated axial ligands at one or both metal sites.^[6–9,11,12] The binding of an axial ligand changes the coordination sphere at the metal site to square-pyramidal thus rendering such PW complexes paramagnetic. A search in the Cambridge Structural Database revealed that in *O,O*-, *S,O*- and *S,S*-bridged Ni₂-PWs, the {NiO₄} sites are always coordinated by an axial ligand, while the {NiS₄} are not.^[14] *S,N*-Bridged Ni₂-PWs have been reported either with^[11] or without^[12,15] axially bound donor ligands. To the best of our knowledge, in none of those both situations have been realized within a given paddlewheel. However, this would be highly interesting as it offers the possibility for molecular, magnetic switching triggered by

*] Dr. K. M. Fürpaß, Dr. L. M. Peschel, Prof. Dr. J. A. Schachner, Prof. Dr. F. Belaj, Prof. Dr. N. C. Mösch-Zanetti
Institute of Chemistry, University of Graz
Schubertstrasse 1, 8010 Graz (Austria)
E-mail: nadia.moesch@uni-graz.at

Prof. Dr. S. M. Borisov
Institute of Analytical Chemistry and Food Chemistry, Graz University of Technology
Stremayrgasse 9, 8010 Graz (Austria)

Prof. Dr. H. Krenn
Institute of Physics, University of Graz
Universitätsplatz 5, 8010 Graz (Austria)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
<https://doi.org/10.1002/anie.202102149>.

© 2021 The Authors. Angewandte Chemie International Edition published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

a donor ligand. Such a magnetic bistability has so far been mostly observed in tailored solid state materials, where cooperative effects (e.g. magnetic coupling or lattice interactions) of a large number of magnetic centers may cause a hysteresis between two spin states.^[16] The limited control over structural parameters, as well as crystal lattice or long-range order breakdowns, together with a sometimes unfavorable low temperature window of hysteresis, remain drawbacks for such solid state materials.^[17,18] In contrast comparatively few examples of molecules in solution showing magnetic bistability devoid of cooperative effects have been disclosed.^[18–21] An interesting example of a fully reversible magnetochemical switching molecule was reported some years ago where a Ni^{II} porphyrin complex with a tethered azo-pyridine linker can adopt two magnetic states depending on light.^[20] Irradiation causes isomerization within the azo-group where the *cis*-configuration allows the pyridine moiety to coordinate to the Ni^{II} center, thereby inducing the magnetochemical switching. Furthermore, magnetic bistability was recently reported for a mononuclear, square planar Ni^{II}-complex in the solid state, in which reversible axial coordination of methanol vapors triggered magnetochemical switching.^[21] Additionally, the complex displayed highly methanol-selective vapochromism for the two different spin states.

Here, the synthesis of complex [Ni₂(Pn)₄] (**2**) is reported, which represents the first example of a Ni₂-PW complex capable of reversibly binding NH₃, both in the solid state and in solution. The coordination of NH₃ is accompanied by a change of color (dark brown **2** to brown-red **2**·NH₃, Figure 2) and magnetism (switching from diamagnetic **2** to paramagnetic **2**·NH₃, Figure 3). The reversibility of the observed switching qualifies **2** as a potential probe for ammonia detection.^[22] The sensing ability of **2** is also realized when coated in thin polyurethane films (Hydromed D4, vide infra).

Results and Discussion

Complex **2** is accessible by a step-wise assembly via mononuclear Ni^{II} precursor [NiCl₂(PnH)₄] (**1**) (Scheme 1). *In-situ* deprotonation of **1** with a base (e.g. NaH, NEt₃) in ethanol or acetonitrile and subsequent addition of one equivalent of NiCl₂ yielded diamagnetic PW complex **2** in analytically pure form as a microcrystalline dark brown solid. The crystalline material consists of an isomeric mix of (2,2)-, (3,1)- and (4,0)-isomers (Figure S4), as observed by ¹H and ¹³C NMR spectroscopy (Figure S1 and S2). When aqueous NH₃ was used as base, a dark red-brown solid was obtained which could be identified as the paramagnetic Ni₂-PW complex [Ni₂(Pn)₄(NH₃)] (**2**·NH₃). The ¹H NMR spectrum of **2**·NH₃ shows broad, downfield shifted signals due to its paramagnetism. Magnetic susceptibility measurements with a Gouy balance ($\mu_{\text{eff}} = 2.85$) revealed two unpaired electrons (Table S1). We therefore conclude that upon exposure to NH₃ a full isomerization to the (4,0)-isomer occurs, finally giving **2**·NH₃.

Single-crystal X-ray diffraction analysis allowed unambiguous determination of the molecular structures of the Ni₂-

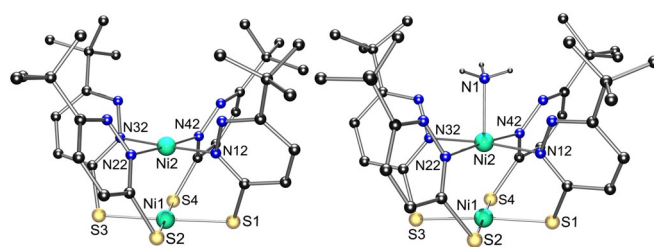


Figure 1. Molecular views of, left: [Ni₂(Pn)₄] (**2**) and right: [Ni₂(Pn)₄(NH₃)] (**2**·NH₃).^[24] Hydrogen atoms except those of NH₃ are omitted for clarity. The atoms are drawn with arbitrary radii.

PW **2** and **2**·NH₃ (Figure 1).^[24] In the solid state **2** and **2**·NH₃ show the well-established PW core.

The Ni atoms in **2** are located in close proximity to each other (Ni–Ni 2.4626(5) Å), corresponding to the shortest Ni···Ni distance reported for *S,N*-bridged Ni₂-PWs. Previously reported Ni–Ni bond distances are at 2.648(2) Å in [Ni₂(tzt)₄] (tzt = thiazoline-2-thione)^[11] and 2.574(2) Å in [Ni₂(mim^{tBu})₄] (mim^{tBu} = *tert*-butylimidazol-thione).^[12] Coordination of NH₃ to the PW framework results in an elongation of the Ni–Ni distance to 2.5008(2) Å in **2**·NH₃. In the penta-coordinate NiN₄NH₃-moiety of **2**·NH₃ the bound NH₃ has assumed the apical position (Ni–NH₃: 2.0471(10) Å). Ni–S bonds are significantly shortened and Ni–N bonds elongated compared to **2**.

Addition of both, aqueous ammonia to **2** in solution (e.g. in CHCl₃) or gaseous NH₃ to solid **2**, results in immediate formation of **2**·NH₃, accompanied by a change of spectral as well as magnetic properties. The apparent color change from dark brown **2** to brown-red **2**·NH₃ is evidenced by a shift of λ_{max} from 532 nm (**2**) to 518 nm (**2**·NH₃) in the UV/Vis spectra in acetonitrile (Figure 2, left). This unusual uptake of ammonia from both aqueous and gaseous sources was further investigated with respect to its reversibility. A thermogravimetric analysis (TGA) experiment of **2**·NH₃ showed a loss of approx. 3 wt % between 70 °C and 120 °C, consistent with loss of one NH₃ molecule. Upon further heating, no significant change in weight occurs up to 320 °C. Thereafter, a weight loss of 34 wt % was observed indicating thermal decomposition of complex **2**. Accordingly, solid **2**·NH₃ was found to re-convert to **2** at 110 °C under dynamic vacuum within one hour. ¹H NMR spectroscopy confirms the coordination and release

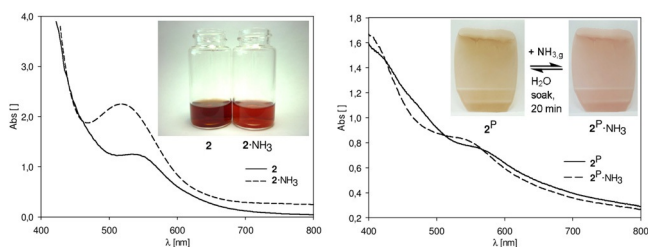


Figure 2. Left: UV/Vis spectrum of **2** and **2**·NH₃ dissolved in acetonitrile ($c = 0.02$ mM); Inset: photographic images of 0.8 mg mL⁻¹ solution of **2** (left vial) and **2**·NH₃ (right vial) in acetonitrile. Right: UV/Vis spectrum of encapsulated **2**^P and **2**^P·NH₃ (10 wt % **2** in Hydromed D4, 7.5 μ m thick); Inset: photographic images of the foils showing reversible uptake and release of NH₃ vapors.

of NH_3 without decomposition of the PW-core (Figure S3). It is interesting to note that the addition of aqueous ammonia to **2** is selective for NH_3 over H_2O . The addition of water to **2** leads in principle to the analogous aqua complex $2\cdot\text{H}_2\text{O}$. However, the coordination seems to be far weaker, as magnetic susceptibility measurements of the isolated materials always showed less than two unpaired electrons, indicating that only mixtures of **2** and $2\cdot\text{H}_2\text{O}$ were obtained.

The potential of **2** as a molecular probe for NH_3 was explored by encapsulation in a suitable hydrogel and subsequent foil formation (2^{P}). Thin foils containing 5, 10 or 20 wt % of **2** were prepared by dissolving the complex and the commercially available polyurethane hydrogel Hydromed D4 in CHCl_3 and knife-coating of the resulting solution onto a transparent poly(ethylene terephthalate) support to give a sensing film of about to $7.5\ \mu\text{m}$ in thickness. The foils are stable in water with no noticeable leaching of **2** and are permeable to NH_3 . Similar to bulk **2**, the 2^{P} foils react with NH_3 vapors forming $2^{\text{P}}\cdot\text{NH}_3$ under color change. Also dipping the foil into aqueous NH_3 solutions (concentration range from 19.6 to 0.03 M NH_3) caused immediate color change (Figure 2, right).

The foils are thin enough to be directly measured in a quartz cuvette in the UV/Vis photometer. In order to test the stability of 2^{P} under repeated NH_3 exposure and removal, the foils were dipped in an aqueous NH_3 (35%) solution (changing color to brown-red). In contrast to $2\cdot\text{NH}_3$, which is completely insoluble in H_2O , the NH_3 in $2^{\text{P}}\cdot\text{NH}_3$ can be easily removed by soaking the foil for 20 min in 200 mL of deionized H_2O (changing color back to dark brown). After each cycle a UV/Vis spectrum was acquired and compared to pristine 2^{P} proving that at least nine cycles of NH_3 coordination and removal are possible without apparent decomposition of 2^{P} (Figure S5).

In order to further probe the magnetic properties of **2** and $2\cdot\text{NH}_3$, the complexes were investigated by SQUID magnetometry. Magnetic susceptibility data was collected in dichloromethane in the temperature range from 300 to 2.7 K at a magnetic field of 70000 Oe. The CH_2Cl_2 -solvent is frozen below 176 K and contributes to a sizeable temperature-independent diamagnetic background for $T < 173\ \text{K}$, which has to be carefully subtracted from the total magnetic signal.

The utmost sensitivity of the SQUID magnetometer allows a correct determination of the magnetic behavior in switching from the diamagnetic sample **2** (Figure 3b) to paramagnetic $2\cdot\text{NH}_3$, by up-scaling the observed paramagnetic signal to the molar susceptibility $\chi_{\text{M}}T$ (Figure 3b). A high magnetic field of 70000 Oe was applied to saturate the sample with its characteristic turn-down of $\chi_{\text{M}}T$ at low temperatures ($< 20\ \text{K}$; Figure 3b). In contrast, the diamagnetism remains constant (level set to zero). The influence of a ligand field (D) has been included in the simulation. The approach to the limiting value of $1\ \text{cm}^3\ \text{K mol}^{-1}$ proves that the bi-nuclear Ni-complex $2\cdot\text{NH}_3$ consists of only one paramagnetic Ni-atom ($S=1$) near the NH_3 -site, exposed to a weak ligand field of $D = 15\ \text{cm}^{-1}$, the other Ni-atom remains diamagnetic.^[1] No evidence for a Ni-Ni bond could be observed. For **2** both Ni-atoms reside in a square planar surrounding with vanishing spin ($S=0$), thus being diamag-

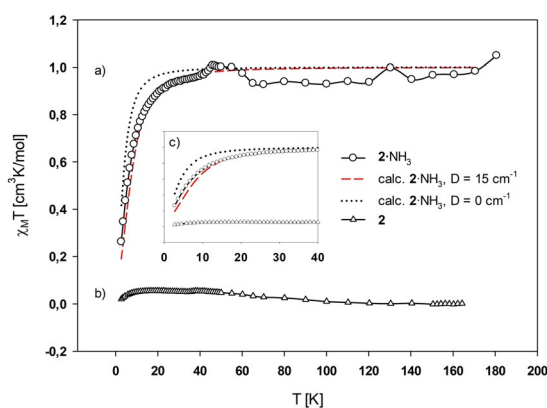


Figure 3. a) Plots of measured (circles) Curie constants $\chi_{\text{M}}T$ versus T of $2\cdot\text{NH}_3$ and calculated $\chi_{\text{M}}T$ with ligand field $D=0\ \text{cm}^{-1}$ (black dotted line) and $D=15\ \text{cm}^{-1}$ (red dashed line). b) Plot of measured (triangles) Curie constants $\chi_{\text{M}}T$ versus T of **2**. c) Expansion of the temperature range $T < 40\ \text{K}$ demonstrating the accuracy of the determination of the ligand field (D) on the mono-atomic Ni-spin $S=1$ in sample $2\cdot\text{NH}_3$.

netic and independent on temperature (Figure 3b). In the simulation the randomness of all spatial paddlewheel orientations with respect to the magnetic field has been considered.

Conclusion

In conclusion, we succeeded in synthesizing a novel Ni_2 -PW complex (**2**) with interesting vapochromic properties and magnetochemical switching of spin states upon exposure to aqueous or gaseous ammonia. The reaction of diamagnetic $[\text{Ni}_2(\text{Pn})_4]$ (**2**) to paramagnetic $[\text{Ni}_2(\text{Pn})_4(\text{NH}_3)]$ ($2\cdot\text{NH}_3$) is the first report of a reversible, magnetically tunable PW system, that features NH_3 uptake and release under mild reaction conditions without a collapse of the PW core. Both **2** and $2\cdot\text{NH}_3$ are fully characterized including single crystal X-ray diffraction analysis and SQUID magnetometry. Furthermore, **2** can be easily incorporated into thin polyurethane foils (2^{P}) under complete retention of its reversible NH_3 sensing capabilities.

Acknowledgements

The authors gratefully acknowledge Prof. C. Slugovc from the Graz University of Technology for providing a TGA measurement of complex $2\cdot\text{NH}_3$ and support from NAWI Graz.

Conflict of interest

The authors declare no conflict of interest.

Keywords: ammonia · nickel complexes · paddlewheel complexes · spin-state switching · vapochromism

- [1] a) F. A. Cotton, C. A. Murillo, R. A. Walton, *Multiple bonds between metal atoms*, Springer Science and Business Media, New York, **2005**; b) M. Köberl, M. Cokoja, W. A. Herrmann, F. E. Kühn, *J. Chem. Soc. Dalton Trans.* **2011**, *40*, 6834–6859; c) N. J. Patmore in *Organometallic Chemistry, Vol. 36* (Eds.: I. J. S. Fairlamb, J. M. Lynam), Royal Society of Chemistry, Cambridge, **2010**; d) E. A. Hillard, *Curr. Inorg. Chem.* **2013**, *3*, 112–143; e) M. Cortijo, R. González-Prieto, S. Herrero, J. L. Priego, R. Jiménez-Aparicio, *Coord. Chem. Rev.* **2019**, *400*, 213040; f) J. Hansen, H. M. L. Davies, *Coord. Chem. Rev.* **2008**, *252*, 545–555; g) J. Campos, *Nat. Rev. Chem.* **2020**, *4*, 696–702.
- [2] a) S. Holler, M. Tüchler, F. Belaj, L. F. Veiros, K. Kirchner, N. C. Mösch-Zanetti, *Inorg. Chem.* **2016**, *55*, 4980–4991; b) G. Nuss, A. Ozwirk, B. N. Harum, G. Saischek, F. Belaj, N. C. Mösch-Zanetti, *Eur. J. Inorg. Chem.* **2012**, 4701–4707; c) G. Nuss, G. Saischek, B. N. Harum, M. Volpe, F. Belaj, N. C. Mösch-Zanetti, *Inorg. Chem.* **2011**, *50*, 12632–12640; d) G. Nuss, G. Saischek, B. N. Harum, M. Volpe, K. Gatterer, F. Belaj, N. C. Mösch-Zanetti, *Inorg. Chem.* **2011**, *50*, 1991–2001; e) M. Tüchler, F. Belaj, G. Raber, D. Neshchadin, N. C. Mösch-Zanetti, *Inorg. Chem.* **2015**, *54*, 8168–8170; f) M. Tüchler, S. Holler, S. Rendl, N. Stock, F. Belaj, N. C. Mösch-Zanetti, *Eur. J. Inorg. Chem.* **2016**, 2609–2614; g) S. Holler, M. Tüchler, B. G. Steller, F. Belaj, L. F. Veiros, K. Kirchner, N. C. Mösch-Zanetti, *Inorg. Chem.* **2018**, *57*, 6921–6931.
- [3] M. Cortijo, P. Delgado-Martínez, R. González-Prieto, S. Herrero, R. Jiménez-Aparicio, J. Perles, J. L. Priego, M. R. Torres, *Inorg. Chim. Acta* **2015**, *424*, 176–185.
- [4] a) C. Furlani, M. L. Luciani, *Inorg. Chem.* **1968**, *7*, 1586–1592; b) M. Bonamico, G. Dessy, V. Fares, *J. Chem. Soc. Dalton Trans.* **1977**, 2315–2319; c) M. Bonamico, G. Dessy, V. Fares, *J. Chem. Soc. D* **1969**, 1107–1108; d) A. Kobayashi, T. Kojima, R. Ikeda, H. Kitagawa, *Inorg. Chem.* **2006**, *45*, 322–327.
- [5] C. Bellitto, G. Dessy, V. Fares, *Inorg. Chem.* **1985**, *24*, 2815–2820.
- [6] F. P. Dwyer, D. P. Mellor, *J. Am. Chem. Soc.* **1941**, *63*, 81–83.
- [7] F. A. Cotton, M. Matusz, R. Poli, *Inorg. Chem.* **1987**, *26*, 1472–1474.
- [8] F. A. Cotton, M. Matusz, R. Poli, X. Feng, *J. Am. Chem. Soc.* **1988**, *110*, 1144–1154.
- [9] C. Lin, J. D. Protasiewicz, T. Ren, *Inorg. Chem.* **1996**, *35*, 7455–7458.
- [10] a) G. A. Melson, N. P. Crawford, B. J. Geddes, *Inorg. Chem.* **1970**, *9*, 1123–1126; b) G. A. Melson, P. T. Greene, R. P. Bryan, *Inorg. Chem.* **1970**, *9*, 1116–1122.
- [11] E. S. Raper, A. M. Britton, W. Clegg, *Inorg. Chim. Acta* **1989**, *166*, 171–172.
- [12] K. Pang, J. S. Figueroa, I. A. Tonks, W. Sattler, G. Parkin, *Inorg. Chim. Acta* **2009**, *362*, 4609–4615.
- [13] T. R. Brown, B. S. Dolinar, E. A. Hillard, R. Clérac, J. F. Berry, *Inorg. Chem.* **2015**, *54*, 8571–8589.
- [14] A. Nimthong-Roldán, J. L. Guillet, J. McNeely, T. J. Ozumerzifon, M. P. Shores, J. A. Golen, A. L. Rheingold, L. H. Doerrer, *Dalton Trans.* **2017**, *46*, 5546–5557.
- [15] a) M. E. Nikiforova, M. O. Talismanova, G. G. Aleksandrov, S. K. Kotovskaya, A. A. Sidorov, V. M. Novotortsev, V. N. Ikorskii, V. N. Charushin, I. L. Eremenko, I. I. Moiseev, *Russ. Chem. Bull.* **2006**, *55*, 2181–2186; b) S.-D. Han, X.-H. Miao, S.-J. Liu, X.-H. Bu, *Dalton Trans.* **2015**, *44*, 560–567.
- [16] J. Larionova, L. Salmon, Y. Guari, A. Tokarev, K. Molvinger, G. Molnár, A. Bousseksou, *Angew. Chem. Int. Ed.* **2008**, *47*, 8236–8240; *Angew. Chem.* **2008**, *120*, 8360–8364.
- [17] a) K. S. Murray, C. J. Kepert in *Topics in Current Chemistry, Vol. 233* (Eds.: P. Güttlich, Y. Garcia), Springer, Berlin, **2004**; b) O. Sato, J. Tao, Y.-Z. Zhang, *Angew. Chem. Int. Ed.* **2007**, *46*, 2152–2187; *Angew. Chem.* **2007**, *119*, 2200–2236; c) J. A. Real, A. B. Gaspar, M. C. Munoz, *Dalton Trans.* **2005**, 2062–2079.
- [18] M. M. Khusniyarov, *Chem. Eur. J.* **2016**, *22*, 15178–15191.
- [19] a) M. Dommaschk, V. Thoms, C. Schutt, C. Nather, R. Puttreddy, K. Rissanen, R. Herges, *Inorg. Chem.* **2015**, *54*, 9390–9392; b) S. Thies, H. Sell, C. Bornholdt, C. Schutt, F. Kohler, F. Tuczek, R. Herges, *Chem. Eur. J.* **2012**, *18*, 16358–16368; c) S. Thies, H. Sell, C. Schütt, C. Bornholdt, C. Näther, F. Tuczek, R. Herges, *J. Am. Chem. Soc.* **2011**, *133*, 16243–16250; d) M. P. Shores, C. M. Klug, S. R. Fiedler in *Spin-Crossover Materials: Properties and Applications* (Ed.: M. A. Halcrow), Wiley, Hoboken, **2013**.
- [20] S. Venkataramani, U. Jana, M. Dommaschk, F. D. Sonnichsen, F. Tuczek, R. Herges, *Science* **2011**, *331*, 445–448.
- [21] P. Kar, M. Yoshida, Y. Shigeta, A. Usui, A. Kobayashi, T. Minamidate, N. Matsunaga, M. Kato, *Angew. Chem. Int. Ed.* **2017**, *56*, 2345–2349; *Angew. Chem.* **2017**, *129*, 2385–2389.
- [22] B. Timmer, W. Olthuis, A. van den Berg, *Sens. Actuators B* **2005**, *107*, 666–677.
- [23] J.-N. Rebilly, G. Charron, E. Riviere, R. Guillot, A.-L. Barra, M. D. Serrano, J. van Slageren, T. Mallah, *Chem. Eur. J.* **2008**, *14*, 1169–1177.
- [24] Deposition Numbers 1536919, 1536920, and 1536921 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Manuscript received: February 10, 2021

Accepted manuscript online: March 26, 2021

Version of record online: May 3, 2021