High-Temperature Spin Crossover in a Mononuclear Six-Coordinate Cobalt(II) Complex

Joanna Palion-Gazda,[†] Anna Świtlicka-Olszewska,[†] Barbara Machura,*[,†] Thais Grancha,[‡] Emilio Pardo,[‡] Francesc Lloret,[‡] and Miguel Julve*[,‡]

[†]Department of Crystallography, Institute of Chemistry, University of Silesia, 9th Szkolna Street, 40006 Katowice, Poland

[‡]Departament de Química Inorgànica, Instituto de Ciencia Molecular (ICMol), Universitat de València, 46980 Paterna, València, Spain

S *Supporting Information*

ABSTRACT: The six-coordinate cobalt(II) complex of formula $[Co(tppz)_2](tcm)_2$ exhibits a thermally induced spin-crossover behavior from a high spin ($S = {}^3/_2$) at higher temperatures to a low spin ($S = {}^1/_2$) at lower temperatures, with the low-spin phase being achieved at $T \leq 200$ K.

Although the preparation of the 2,3,5,6-tetrakis(2-pyridyl)-pyrazine ligand (hereafter denoted as tppz) was first reported in 1959 by Goodwin and Lions,[1] the first structural report of a tppz-containing metal complex appeared only 20 years ago.[2] The apparent lack of interest in the investigation of the coordination chemistry of such a prototype of a ligand with two 2,2′:6′,2″-terpyridine (terpy) domains was based the assumption that tppz would coordinate to only one metal ion because the four pendant 2-pyridyl rings could not be coplanar with the central pyrazine ring. In spite of confirmation of this lack of coplanarity,[3] several studies have revealed the great versatility of this ligand in complex formation, adopting a variety of terminal (bidentate α or γ and tridentate) and bridging [bis(bidentate) α or γ, bis(bidentate) α and γ, and bis(tridentate)] coordination modes.[4] Applications of its metal complexes as sensors,[5] molecular wires,[6] biochemical and DNA binding properties,[7] supramolecular films,[8] precursors to synthesize carbon-supported catalysts (Fe–N$_x$/C),[9] and builders for the rational design of extended structures containing $[Mo_5O_{15}-(HOPO_3)_2]^{4-},$[10a] $[Mo_5O_{15}(O_3PR)_2]^{4-},$[10b,c] and $Mo_8O_{26}{}^{4-}$[10d–f] clusters have been reported.

Another property of tppz is its ability to mediate relatively large magnetic interactions between paramagnetic centers separated by more than 6.4 Å in the tppz-bridged metal complexes.[4b,11–14] Interestingly, the $[Fe(tppz)_2]^{2+}$ entity is a low-spin (LS) species,[4c,12] with the tridentate tppz molecule behaving as a strong-field ligand versus iron(II) in analogy with the parent terpy ligand.[15] Keeping in mind the greater mean spin-pairing energy for cobalt(II) relative to that for iron(II) for comparable six-coordinate complexes,[16] the possibility of the $[Co(tppz)_2]^{2+}$ species to undergo a thermally induced spin transition deserves to be explored. It is worthe noting that the majority of spin-crossover (SCO) compounds characterized so far deal with iron(II) and iron(III) compounds, whereas those with cobalt(II) have been investigated to a lesser extent.[15b]

Herein we present a preliminary magnetostructural study on the cobalt(II) complex of formula $[Co(tppz)_2](tcm)_2$ (**1**; tcm = tricyanomethanide anion), which exhibits a thermally induced spin transition with a change of the electron configuration $t_{2g}{}^6e_g{}^1$ (^2E_g, LS) $\Leftrightarrow$ $t_{2g}{}^5e_g{}^2$ ($^4T_{1g}$, HS), the LS phase being achieved at $T \leq 200$ K.

The crystal structure of **1** has been solved at 293 K (Table S1 in the Supporting Information, SI). It consists of discrete $[Co(tppz)_2]^{2+}$ cations and tcm$^-$ counteranions (Figure 1).
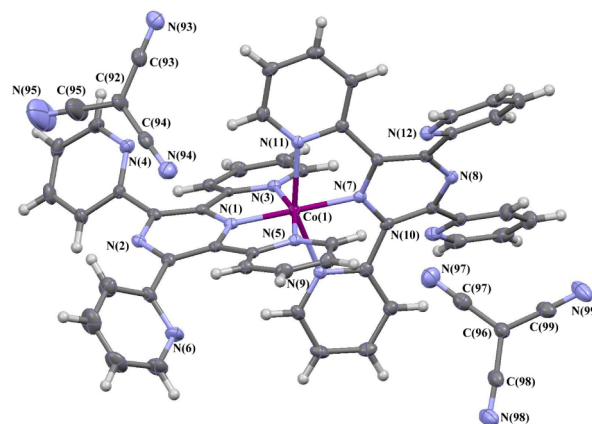

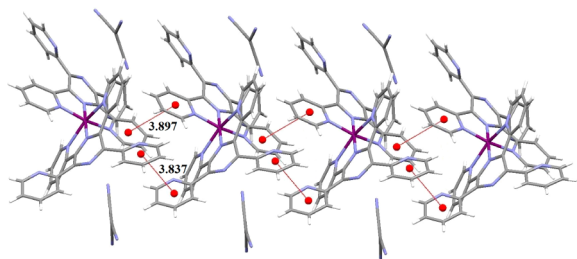**Figure 1.** Perspective view of **1** (50% probability ellipsoids).

Each *mer*-tridentate tppz ligand coordinates to the cobalt(II) ion equatorially via two pyridyl donors and axially via the pyrazine, completing the coordination sphere. The value of the N-(pyrazine)–Co–N(pyrazine) angle [179.56(8)°] is quasi-linear, whereas those of the remaining *trans* N–Co–N angles [156.80(7)° and 163.15(8)° for N(9)–Co(1)–N(11) and N(3)–Co(1)–N(5), respectively] reflect the steric constraints imposed by the rigidity of the tridentate tppz ligand. The dihedral angle between the least-squares planes defined by the coordinated pyridine and pyrazine rings of the two ligands is 86.35°, and the distortion parameter Σ, defined as the sum of the deviation from 90° of the 12 *cis* angles of the CoN$_6$ octahedron, equals 81.70°. The axial Co–N$_{pyrazine}$ bond lengths [1.865(2) and 1.936(2) Å] are shorter than the Co–N$_{pyridyl}$ ones [1.977(2)–

2.160(2) Å; Table S2 in the SI), forming a compressed octahedral surrounding, as expected for a LS six-coordinate cobalt(II) ion significantly distorted by Jahn−Teller arising from the single e_g electron.[17] The structural parameters of **1** are consistent with a thermal-averaged mixture of HS and LS states for cobalt(II) SCO complexes (see Table S4 in the SI).

The whole ligands are appreciably twisted: the dihedral angles between the N(1)/N(2) pyrazine ring and each of its pyridyl substituents are 43.73(9)°, 45.94(10)°, 14.13(10)°, and 17.39(10)° arranged in order of rings containing N(4), N(6), N(5), and N(3) [to be compared with 23.52(11)°, 24.74(11)°, 31.31(11)°, and 35.00(10)° for the N(11), N(9), N(10), and N(12) rings in the tppz ligand containing the N(7)/N(8) pyrazine group]. The pyrazine rings from the two tppz ligands are significantly puckered, with maximum atomic deviations from a best mean plane being 0.0810(16) and 0.1313(17) Å at the C(3) and C(26) atoms, respectively. Low-energy conformations of free tppz molecules are predicted to have each pyridyl ring twisted from coplanarity with the pyrazine group roughly 50°.[4d] $\pi-\pi$-type interactions involving the pyridyl rings of the tppz ligands, which connect the [Co(tppz)$_2$]$^{2+}$ cations into a chain with cobalt(II) ions separated by 8.940 Å, contribute to stabilization of the structure {values of 3.8971(15) and 3.8366(16) Å for the Cg1[N(5)−C(20)−C(24)]···Cg2^i[N-(3)−C(8)−C(12)] and Cg3[N(12)−C(39)−C(43)]···Cg4^i[N-(10)−C(34)−C(38)] centroids, respectively; i, −1 + x, y, z; Figure 2}. Additionally, the tcm$^-$ anions are linked to the
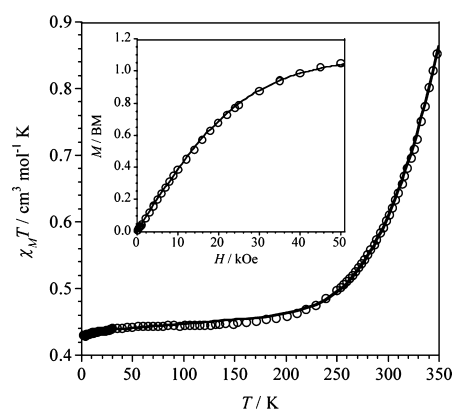

Figure 2. View of a fragment of the supramolecular chain in **1** arising from weak $\pi-\pi$-type interactions.

complex cation via very weak C−H···N-type interactions (Table S3 in the SI), leading to a three-dimensional supramolecular network. These intramolecular interactions seem to generate additional chemical pressure to stabilize the LS state of cobalt(II) in **1**. This is reflected by the low value of the C parameter (see below). A crucial role of lattice interactions in driving the SCO behavior has been evidenced previously.[15a,18]

The $\chi_M T$ versus T plot for **1** [χ_M is the magnetic susceptibility per cobalt(II) ion] is shown in Figure 3. $\chi_M T$ is almost constant in the temperature range 1.9−185 K, taking a value of ca. 0.42 cm^3 mol^{-1} K. This value is consistent with the S = $^1/_2$ ground state that follows the Curie−Weiss law with g = 2.12. When the sample is warmed, $\chi_M T$ smoothly increases, attaining a value of 0.85 cm^3 mol^{-1} K at 350 K. This behavior clearly indicates the occurrence of a very incomplete $^1/_2$ (LS) ⇔ $^3/_2$ (HS) conversion at 350 K. The magnetization (M) versus H plot for **1** at 2.0 K (see the inset of Figure 3) corresponds to what is expected for a spin doublet, with the value of M at 5 T (the maximum available field in our magnetometer) tending to a value somewhat above 1.0 μ_B
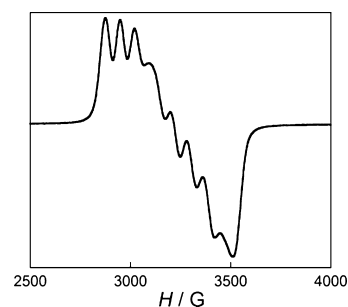
Analysis of the magnetic data of **1** through a theoretical model that considers one doublet state (^{2}E) and one quartet state (^{4}T$_1$) separated by an energy gap E, whose degeneracy is removed by a

Figure 3. $\chi_M T$ versus T plot for **1**: (○) experimental; (—) best-fit curve through a model derived elsewhere.[19] The inset shows the M versus H plot for **1** at 2.0 K.

combination of spin−orbit coupling and first- and second-order Zeeman effects,[19] leads to the following two sets of best-fit parameters: γ = −1.10(1), μ_E = 1.91 μ_B, ζ = 510 cm^{-1}, E = 2015(10) cm^{-1}, and C = 0.075(1) [or γ = −1.49(1), μ_E = 1.86 μ_B, ζ = 450 cm^{-1}, E = 2070(10) cm^{-1}, and C = 0.0105(3)]. γ is a term that lies between −1.5 (weak-field ligand) and −1 (strong-field ligand), μ_E is the effective magnetic moment for the ^{2}E state, ζ is the one-electron spin−orbit coupling constant, E is the energy gap between the ^{4}T and ^{2}E states, and C is the ratio of the vibrational partition functions in the HS and LS states. The calculated curves through both sets of values match very well the experimental data in the whole temperature range explored, and they compare well with those reported for other Co^{II}N$_6$ SCO systems.[20]

X-band electron paramagnetic resonance (EPR) measurements on a polycrystalline sample of **1** at low temperatures consists of a quasi-isotropic feature centered at 3220 G (Figure S2 in the SI; T = 25 K). This signal for a frozen dichloromethane solution of **1** at 4.0 K shows a hyperfine splitting of A = 70 G in the form of eight lines due to coupling to the I = $^7/_2$ nucleus of cobalt, with the g value being 2.12 and a frozen dichloromethane solution (Figure 4).

Figure 4. X-band EPR spectrum of a frozen dichloromethane solution of **1** at 4.0 K.

In summary, the tppz molecule having two potential tridentate sites in *trans* position is a strong-field ligand in its cobalt(II) complexes, as shown by the present magnetostructural investigation on the mononuclear compound **1**. Variable-temperature magnetic susceptibility measurements on a polycrystalline sample and EPR spectroscopy on both solid and frozen dichloromethane solutions of **1** revealed SCO behavior, in agreement with the previous results on the parent

$[Co(terpy)_2]^{2+}$, $[Co(4\text{-terpyridone})_2]^{2+}$, and $[Co(dpzca)_2]$ [terpy = 2,2′:6′,2″-terpyridine, 4-terpyridone = 2,6-bis[2-pyridyl-4($1H$)-pyridone], and Hdpzca = bis(2-pyrazinylcarbonyl)amide] mononuclear species.[16c,21] The LS state in **1** is achieved at T = 185 K with $S = {}^1/_2$, and the HS configuration is far from being completely populated at 350 K, with the value of $\chi_M T$ at this temperature being only 0.85 cm^3 mol^{-1} K (to be compared with values of $\chi_M T$ in the range 2.5–3.0 cm^3 mol^{-1} K for full population of the HS state in the parent terpy- and 4-terpyridone-containing complexes). The influence of the counterion on the spin transition in **1** as well as the use of the $[Co(tppz)_2]^{2+}$ unit as a metalloligand to build SCO heterometallic species will be the subject of further works.

ASSOCIATED CONTENT

ⓢ Supporting Information

Synthesis, crystallographic data (Tables S1–S3), CCDC 999841, structural data for CoN$_6$ SCO systems (Table S4), UV–vis electron spectrum (Figure S1), and X-band EPR spectrum on a solid sample (Figure S2). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors
*E-mail: basia@ich.us.edu.pl.
*E-mail: Miguel.Julve@uv.es.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

REFERENCES

(1) Goodwin, H. A.; Lions, F. *J. Am. Chem. Soc.* **1959**, *81*, 6415–6422.

(2) Graf, M.; Greaves, B.; Stoeckli-Evans, H. *Inorg. Chim. Acta* **1993**, *204*, 239–246.

(3) (a) Padgett, C. W.; Walsh, R. D.; Drake, G. W.; Hanks, T. W.; Pennington, W. T. *Cryst. Growth Des.* **2005**, *5*, 745–753. (b) Greaves, B.; Stoeckli-Evans, H. *Acta Crystallogr.* **1992**, *C48*, 2269–2271. (c) Bock, H.; Vaupel, T.; Näther, C.; Ruppert, K.; Havlas, Z. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 299–301.

(4) (a) Machura, B.; Palion, J.; Mrozinski, J.; Kalinska, B.; Amini, M.; Najafpour, M. M.; Kruszynski, R. *Polyhedron* **2013**, *53*, 132–143. (b) Yuste, C.; Cañadillas-Delgado, L.; Ruiz-Pérez, C.; Lloret, F.; Julve, M. *Dalton Trans.* **2010**, *39*, 167–179. (c) Toma, L. M.; Armentano, D.; De Munno, G.; Sletten, J.; Lloret, F.; Julve, M. *Polyhedron* **2007**, *26*, 5263–5270. (d) Padgett, C. W.; Pennington, W. T.; Hanks, T. W. *Cryst. Growth Des.* **2005**, *5*, 737–744.

(5) (a) Maskus, M.; Abruña, H. D. *Langmuir* **1996**, *12*, 4455–4462. (b) Yuasa, J.; Fukuzumi, S. *J. Am. Chem. Soc.* **2006**, *128*, 15976–15977. (c) Yuasa, J.; Fukuzumi, S. *J. Am. Chem. Soc.* **2008**, *130*, 566–575. (d) Hadadzadeh, H.; Hosseinian, S. R.; Fatemi, S. J. A. *Polyhedron* **2009**, *28*, 2776–2784.

(6) (a) Fantacci, S.; De Angelis, F.; Wang, J.; Bernhard, S.; Selloni, A. *J. Am. Chem. Soc.* **2004**, *126*, 9715–9723. (b) Flores-Torres, S.; Hutchison, G. R.; Soltzberg, L. J.; Abruña, H. D. *J. Am. Chem. Soc.* **2006**, *128*, 1513–1522. (c) Carlson, C. N.; Kuehl, C. J.; Da Re, R. E.;

Veauthier, J. M.; Schelter, E. J.; Milligan, A. E.; Scott, B. L.; Bauer, E. D.; Thompson, J. D.; Morris, D. E.; John, K. D. *J. Am. Chem. Soc.* **2006**, *128*, 7230–7241.

(7) (a) Rubino, S.; Portanova, P.; Girasolo, A.; Galvaruso, G.; Orecchio, S.; Stoco, G. C. *Eur. J. Med. Chem.* **2009**, *44*, 1041–1048. (b) Haghighi, F. H.; Hadadzadeh, H.; Darabi, F.; Jannesari, Z.; Ebrahimi, M.; Khayamian, T.; Salimi, M.; Rudbari, H. A. *Polyhedron* **2013**, *65*, 16–30.

(8) Alves, W. A.; Pfaffen, V.; Ortiz, P. I.; Córdoba de Torresi, S. I.; Torressi, R. M. *J. Braz. Chem. Soc.* **2008**, *19*, 651–659.

(9) Velázquez-Valenzuela, A.; Zhang, L.; Wang, L.; Cabot, P. L.; Brillas, E.; Tsay, K.; Zhang, J. *Electrochim. Acta* **2011**, *56*, 4744–4752.

(10) (a) Burkholder, E.; Zubieta, J. *Chem. Commun.* **2001**, 2056–2057. (b) Armatas, N. G.; Allis, D. G.; Prosvirin, A.; Carnutu, G.; O'Connor, C. J.; Dunbar, K.; Zubieta, J. *Inorg. Chem.* **2008**, *47*, 832–854. (c) Burkholder, E.; Golub, V.; O'Connor, C. J.; Zubieta, J. *Inorg. Chem.* **2003**, *42*, 6729–6740. (d) Hagrman, D.; Hagrman, P.; Zubieta, J. *Inorg. Chim. Acta* **2000**, *300–302*, 212. (e) Boukholder, E.; Zubieta, J. *Solid State Sci.* **2004**, *6*, 1421–1428. (f) Burkholder, E.; Zubieta, J. *Inorg. Chim. Acta* **2005**, *358*, 116–122.

(11) Graf, M.; Stoeckli-Evans, H.; Escuer, A.; Vicente, R. *Inorg. Chim. Acta* **1997**, *257*, 89–97.

(12) Campos-Fernández, C. S.; Smucker, B. W.; Clérac, R.; Dunbar, K. R. *Isr. J. Chem.* **2001**, *41*, 207–218.

(13) Hsu, G.-H.; Cheng, C.-W.; Cheng, S.-C.; Lin, S.-H.; Wei, H.-H.; Lee, C.-J. *Polyhedron* **2005**, *24*, 487–494.

(14) (a) Yuste, C.; Armentano, D.; Marino, N.; Cañadillas-Delgado, L.; Delgado, F. S.; Ruiz-Pérez, C.; Rillema, D. P.; Julve, M. *Dalton Trans.* **2008**, 1583–1596. (b) Carranza, J.; Sletten, J.; Brennan, C.; Lloret, F.; Cano, J.; Julve, M. *Dalton Trans.* **2004**, 3997–4005. (c) Carranza, J.; Brennan, C.; Sletten, J.; Clemente-Juan, J. M.; Lloret, F.; Julve, M. *Inorg. Chem.* **2003**, *42*, 8716–8727.

(15) (a) Halcrow, M. A. *Chem. Soc. Rev.* **2011**, *40*, 4119–4142. (b) García, Y.; Niel, V.; Muñoz, M. C.; Real, J. A. *Top. Curr. Chem.* **2004**, *233*, 229–257. (c) Baker, A. T.; Goodwin, H. A. *Aust. J. Chem.* **1985**, *38*, 207–214. (d) Goodwin, H. A. *Coord. Chem. Rev.* **1976**, *18*, 293–325.

(16) (a) Gütlich, P. *Eur. J. Inorg. Chem.* **2013**, 581–591. (b) Hayami, S.; Karim, M. R.; Lee, Y. H. *Eur. J. Inorg. Chem.* **2013**, 683–696. (c) Krikokapic, K.; Zerara, M.; Daku, M. L.; Vargas, A.; Enachescu, C.; Ambrus, C.; Tregenna-Piggott, P.; Amstutz, N.; Krausz, E.; Hauser, A. *Coord. Chem. Rev.* **2007**, *251*, 364–378.

(17) (a) Goodwin, H. A. *Top. Curr. Chem.* **2004**, *234*, 23–47. (b) Wu, S.-Q.; Wang, Y.-T.; Cui, A.-L.; Kou, H.-Z. *Inorg. Chem.* **2014**, *53*, 2613–2618. (c) Gass, I. A.; Tewary, S.; Rajaraman, G.; Asadi, M.; Lupton, D. W.; Moubaraki, B.; Chastanet, G.; Létard, J.-F.; Murray, K. S. *Inorg. Chem.* **2014**, *53*, 5055–5066.

(18) (a) Dupouy, G.; Marchivie, M.; Triki, S.; Sala-Pala, J.; Salaün, J.-Y.; Gómez-García, C. J.; Guionneau, P. *Inorg. Chem.* **2008**, *47*, 8921–8931. (b) Schweinfurth, D.; Weisser, F.; Dubrin, D.; Bogani, L.; Sarkar, B. *Inorg. Chem.* **2011**, *50*, 6114–6121. (c) Atmani, Ch.; El Hajj, F.; Benmansur, S.; Marchivie, M.; Triki, S.; Conan, F.; Patinec, V.; Handel, H.; Dupouy, G.; Gómez-García, C. J. *Coord. Chem. Rev.* **2010**, *254*, 1559–1569. (d) Novokov, V. V.; Anayev, I. V.; Pavlov, A. A.; Fedin, M. V.; Lyssenko, K. A.; Voloshin, Y. Z. *J. Phys. Chem. Lett.* **2014**, *5*, 496–500.

(19) Martin, R. L.; White, A. H. *Transition Met. Chem.* **1968**, *4*, 113–198.

(20) Vecchio-Sadus, A. M. *Transition Met. Chem.* **1995**, *28*, 38–45.

(21) (a) Kremer, S.; Henke, W.; Reinen, D. *Inorg. Chem.* **1982**, *21*, 3013–3022. (b) Figgis, B. N.; Kucharski, E. S.; White, A. H. *Aust. J. Chem.* **1983**, *36*, 1537–1561. (c) Galet, A.; Gaspar, A. B.; Muñoz, M. C.; Real, J. A. *Inorg. Chem.* **2006**, *45*, 4413–4422. (d) Echanescu, C.; Krivokapic, I.; Zerara, M.; Real, J. A.; Amstutz, N.; Hauser, A. *Inorg. Chim. Acta* **2007**, *360*, 3945–3950. (e) Kilner, C. A.; Halcrow, M. A. *Dalton Trans.* **2010**, *39*, 9008–9012. (f) Hayami, S.; Komatsu, Y.; Shimizu, T.; Kamihata, H.; Lee, Y. H. *Coord. Chem. Rev.* **2011**, *255*, 1981–1990. (g) Cowan, M. G.; Olguín, J.; Narayanaswamy, S.; Tallon, J. L.; Brooker, S. *J. Am. Chem. Soc.* **2011**, *134*, 2892–2894.