Electronic Supplementary Information

Spin-canted ferromagnetic behaviour and unusual thermal decomposition of $[Co\{MeO(O)CC_6H_4NHC(S)NP(S)(O\textit{i}Pr)_2\}_2]$

Maria G. Babashkina,*[a] Damir A. Safin,[a] Antoine Railliet,[a] Michael Bolte,[b] Anna Brzuszkiewicz,[c] Henryk Kozlowski[c] and Yann Garcia*[a]

[a] *Institute of Condensed Matter and Nanosciences, MOST – Inorganic Chemistry, Université Catholique de Louvain, Place L. Pasteur 1, 1348 Louvain-la-Neuve, Belgium. Fax: +32(0) 1047 2330; Tel: +32(0) 1047 2831; E-mail: maria.babashkina@ksu.ru, yann.garcia@uclouvain.be*

[b] *Institut für Anorganische Chemie J.-W.-Goethe-Universität, Frankfurt/Main, Germany.*

[c] *Faculty of Chemistry, University of Wroclaw, F. Joliot-Curie Str. 14, 50383 Wroclaw, Poland*

Physical measurements

Infrared spectrum (KBr) was recorded with a FTIR-8400S SHIMADZU spectrophotometer in the range 400–3600 cm^{-1}. NMR spectra ($CDCl_3$) were obtained on a Bruker Avance 300 MHz spectrometer at 25 °C. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded at 299.948, and 121.420 MHz, respectively. Chemical shifts are reported with reference to $SiMe_4$ (^1H) and 85% H_3PO_4 ($^{31}P\{^1H\}$). UV-Vis absorption spectrum of a 10^{-4} M solution in CH_2Cl_2 was recorded on a Lambda-35 spectrometer in the range 200–1000 nm. Diffuse reflectance spectra were obtained with a Varian Cary 5E spectrometer using polytetrafluoroethylene (PTFE) as a reference. The spectra were measured on a pure solid to avoid matrix effects. Eventual distortions in the Kubelka-Munk spectra that could result from the study of pure compounds have not been considered because no comparison with absorption spectra was necessary. Simultaneous thermogravimetric (TG) and differential thermal (DTA) analyses were performed by a SDT 2960 Simultaneous DTA-TGA instrument in a dynamic air atmosphere (100 mL min^{-1}) from laboratory temperature to 900 °C with a 10 °C min^{-1} heating rate. Electrospray ionization mass spectra were recorded on a Thermo Fisher Scientific LCQ mass spectrometer on a 10^{-6} M solution in MeOH. The spray voltage was 5 kV. The capillary temperature was 260 °C. Magnetic susceptibility measurements were performed on MPMS-5 Quantum Design instrument in the temperature range 1.9–300 K. Elemental analyses were performed on a Thermoquest Flash EA 1112 Analyzer from CE Instruments.

Synthesis of $[CoL_2]$

A suspension of **HL** (0.390 g, 1 mmol) in MeOH (10 mL) was mixed with a MeOH solution of KOH (0.062 g, 1.1 mmol). A MeOH (10 mL) solution of $Co(NO_3)_2{\cdot}6H_2O$ (0.175 g, 0.6 mmol) was added dropwise under vigorous stirring to the resulting potassium salt. The mixture was stirred at room temperature for a further 3 h and left overnight. The resulting complex was extracted with CH_2Cl_2, washed with water and dried with anhydrous $CaCl_2$.

The solvent was then removed in vacuo. Green crystals were isolated by recrystallisation from a 1:3 mixture of *n*-hexane and *n*-octane.

Yield 0.402 g (96%). IR, ν: 603 (P=S), 1007 (POC), 1533 (SCN), 1591 (C_6H_4), 1695 (C=O), 3247 (NH) cm^{-1}. UV-Vis, λ_{max} (ε, M^{-1} cm^{-1}): 262 (34780), 315 (16423), 387 (10185), 556 (260), 616 (287), 678 (162) nm. ^1H NMR, δ: 1.17 (br. s, 6H, CH_3, Me), 4.63 (br. s, 12H, CH_3, *i*Pr), 6.09 (br. s, 12H, CH_3, *i*Pr), 14.48 (br. S, 8H, C_6H_4), 18.93 (br. s, 4H, OCH), 32.18 (br. s, NH) ppm. $^{31}P\{^1H\}$ NMR, δ: 109.6 ppm. ESI-MS$^+$, *m/z* (*I*, %): 390.93 (12.5) $[HL + H]^+$, 412.99 (17.5) $[HL + Na]^+$, 837.84 (35.7) $[M + H]^+$, 859.95 (100) $[M + Na]^+$, 875.88 (34.2) $[M + K]^+$, 894.76 (44.3) $[M + CH_3OH + Na]^+$, 1284.69 (84.1) $[Co_2L_3]^+$. ESI-MS$^-$, *m/z* (*I*, %): 389.09 (100) $[L]^-$, 835.07 (10.7) $[M - H]^-$. *Anal*. Calc. for $C_{30}H_{44}CoN_4O_8P_2S_4$ (837.80): C 43.01, H 5.29, N 6.69. Found: C 43.08, H 5.22, N 6.74%.

X-Ray crystallography

The X-ray data of **[CoL₂]** at 100 K were collected on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo-Kα. Data reduction and analysis were carried out with the Oxford Diffraction programs.[1,2] The structure was solved by a direct method using the SHELXS-97 program[3] and refined by the full-matrix least-squares method on all F^2 data using the SHELXL-97.[4] Non-hydrogen atoms were refined with anisotropic displacement parameters with the exception of two disordered atoms in isopropyl group. Hydrogen atoms were included from geometry of the molecule. The isopropyl methyl group C19 is disordered over two sites and labeled as C19A and C19B with the occupancies 0.549(6) and 0.451(6), respectively.

The X-ray data of **[CoL₂]** at 173 K were collected on a STOE IPDS-II diffractometer with graphite-monochromatised Mo-Kα radiation generated by a fine-focus X-ray tube operated at 50 kV and 40 mA. The reflections of the images were indexed, integrated and scaled using the X-Area data reduction package.[5] Data were corrected for absorption using the PLATON program.[6] The structure was solved by a direct method using the SHELXS-97 program[7] and refined first isotropically and then anisotropically using SHELXL-97.[7] Hydrogen atoms were revealed from $\Delta\rho$ maps and those bonded to C were refined using appropriate riding models. The hydrogen atom bonded to N was freely refined.

Figures were generated using the Mercury program.[8]

Crystal data for [CoL₂] at 100 K. $C_{30}H_{44}CoN_4O_8P_2S_4$, M_r = 837.80 g mol^{-1}, triclinic, space group *P*–1, a = 10.459(3), b = 11.329(3), c = 17.261(4) Å, α = 78.15(2), β = 84.00(2), γ = 85.35(2)°, V = 1987.0(9) Å^3, Z = 2, ρ = 1.400 g cm^{-3}, μ(Mo-Kα) = 0.772 mm^{-1}, reflections: 25353 collected, 9119 unique, R_{int} = 0.029, R_1(all) = 0.0335, wR_2(all) = 0.0794.

Crystal data for [CoL₂] at 173 K. $C_{30}H_{44}CoN_4O_8P_2S_4$, M_r = 837.80 g mol^{-1}, triclinic, space group *P*–1, a = 10.4743(8), b = 11.3943(9), c = 17.3391(14) Å, α = 78.149(6), β = 84.676(6), γ = 85.234(6)°, V = 2012.2(3) Å^3, Z = 2, ρ = 1.383 g cm^{-3}, μ(Mo-Kα) = 0.762 mm^{-1}, reflections: 33235 collected, 7092 unique, R_{int} = 0.060, R_1(all) = 0.0674, wR_2(all) = 0.1492.

CCDC 893875 (**[CoL$_2$] at 100 K**) and 893876 (**[CoL$_2$] at 173 K**) contain the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

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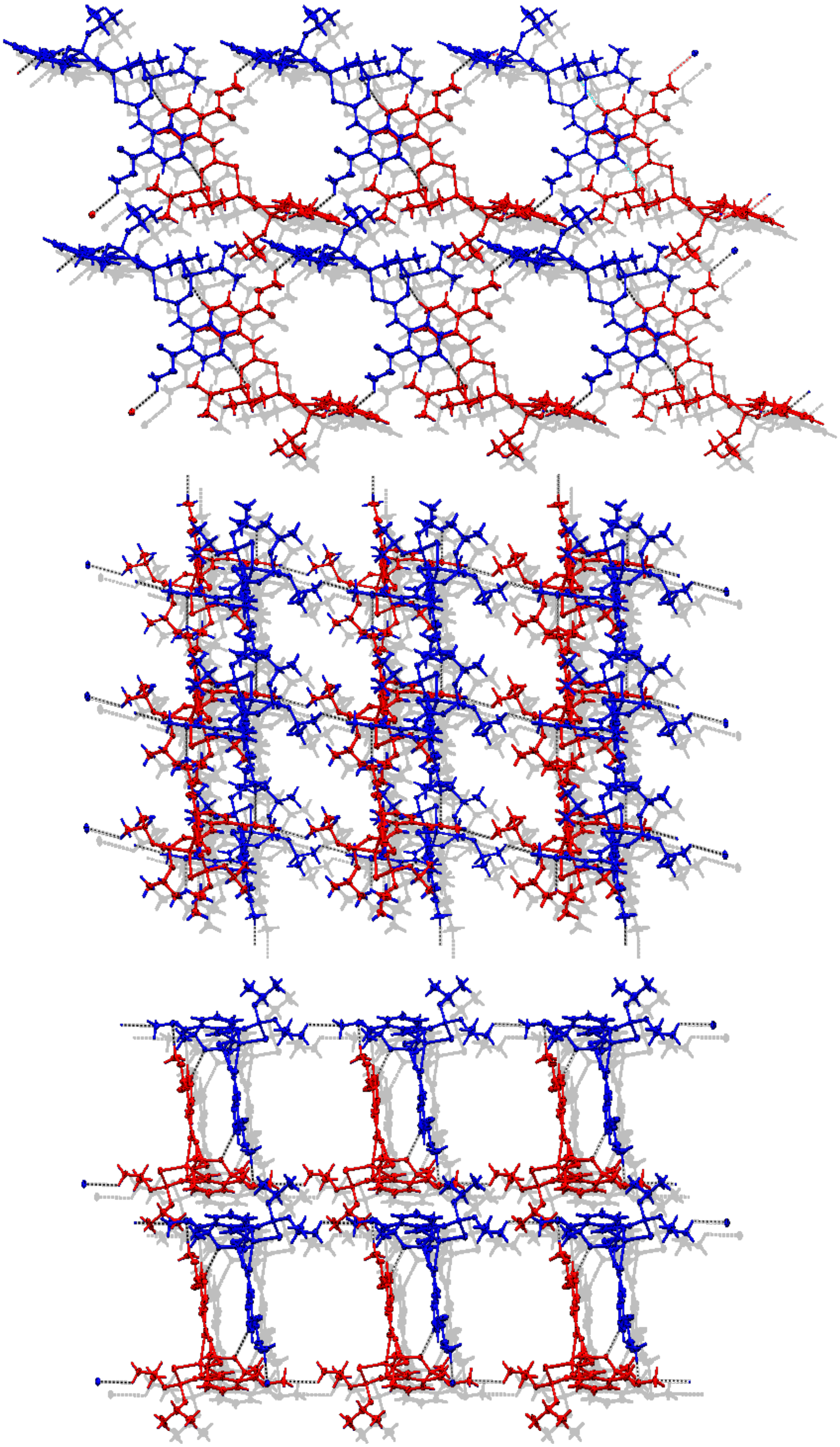

Fig. S1 Thermal ellipsoid (50%) plot of a 3D framework formed by the C–H···N, C–H···O and C–H···S contacts of **[CoL$_2$]** at 100 K (three representative views). The structure of a 3D framework of **[CoL$_2$]** at 173 K is similar.

Table S1. Selected bond lengths (Å) and angles (°) for **[CoL_2]**

	100 K	**173 K**
Bond lengths		
Co–S(C)	2.277(1), 2.280(1)	2.276(1), 2.279(1)
Co–S(P)	2.317(1), 2.329(1)	2.315(1), 2.332(1)
C–S	1.748(2), 1.756 (2)	1.751(3), 1.752(3)
P–S	1.996(1), 1.996(1)	1.993(2), 1.995(1)
P–N	1.611(2), 1.614(1)	1.601(3), 1.608(3)
C–N(P)	1.308(2), 1.308(2)	1.304(4), 1.307(4)
C–N(C)	1.361(2), 1.405(2)	1.362(5), 1.373(5)
Bond angles		
S–Co–S$_{\text{endo.}}$	107.36(2), 107.52(2)	107.43(4), 107.56(4)
S–Co–S$_{\text{exo.}}$	109.29(3), 109.93(2), 111.19(2), 111.55(3)	109.48(4), 109.56(4), 111.38(4), 111.42(4)
Co–S–C	108.26(5), 111.05(5)	108.39(12), 110.80(12)
Co–S–P	96.30(3), 98.77(3)	96.53(4), 98.90(5)
S–C–N(C)	110.63(10), 111.80(10)	110.2(3), 112.2(2)
S–C–N(P)	127.76(11), 128.86(12)	127.9(3), 128.7(3)
S–P–N	117.20(5), 117.33(5)	117.28(12), 117.40(12)
P–N–C	125.54(10), 127.14(11)	125.9(2), 127.8(2)
N–C–N	120.41(13), 120.48(13)	119.9(3), 121.1(3)

Table S2. Hydrogen bond lengths (Å) and angles (°) for **[CoL_2]**

	D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
100 K	N(2)–H(2)···O(4)	0.86	1.91	2.636(2)	141
	N(4)–H(4)···O(8)	0.86	2.03	2.686(2)	133
173 K	N(2)–H(2)···O(4)	0.87(2)	1.88(3)	2.637(5)	145(3)
	N(4)–H(4)···O(8)	0.91(4)	1.90(4)	2.671(4)	141(3)

Table S3. π···π interactions for **[CoL$_2$]**

	Cg(*I*)	Cg(*J*)	Cg(*I*)_Perp (Å)	Cg(*J*)_Perp (Å)
100 K[a]	Cg(3)	Cg(3)$^{\#1}$	3.408	3.408
	Cg(4)	Cg(4)$^{\#2}$	3.370	3.370
173 K[b]	Cg(3)	Cg(3)$^{\#1}$	3.449	3.449
	Cg(4)	Cg(4)$^{\#2}$	3.382	3.382

[a] Symmetry codes: #1 1 – *x*, –*y*, –*z*; #2 2 – *x*, 1 – *y*, 1 – *z*.
[b] Symmetry codes: #1 –*x*, –*y*, –*z*; #2 1 – *x*, 1 – *y*, 1 – *z*.
Cg(3): C(8)–C(9)–C(10)–C(11)–C(12)–C(13), Cg(4): C(23)–C(24)–C(25)–C(26)–C(27)–C(28).

Table S4. Selected weak contact bond lengths (Å) and angles (°) for **[CoL$_2$]**

	D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
100 K	C(3)–H(3A)···S(4)	0.96	2.84	3.688(2)	148
	C(4)–H(4A)···O(2)	0.96	2.56	3.185(2)	123
	C(10)–H(10)···O(3)	0.93	2.37	2.708(2)	101
	C(13)–H(13)···N(1)	0.93	2.30	2.902(2)	122
	C(17)–H(17)···S(3)	0.98	2.84	3.367(2)	115
	C(25)–H(25)···O(7)	0.93	2.34	2.687(2)	101
	C(28)–H(28)···O(3)	0.93	2.32	2.882(2)	119
173 K	C(3)–H(3A)···S(4)	0.98	2.84	3.722(4)	150
	C(4)–H(4A)···O(2)	0.98	2.56	3.193(5)	122
	C(10)–H(10)···O(3)	0.95	2.37	2.715(6)	101
	C(13)–H(13)···N(1)	0.95	2.29	2.893(5)	121
	C(17)–H(17)···S(3)	1.00	2.78	3.372(5)	118
	C(25)–H(25)···O(7)	0.95	2.33	2.676(5)	101
	C(28)–H(28)···O(3)	0.95	2.30	2.884(4)	119