Synthesis, Crystal Molecular Structure, and Magnetic Characteristics of Coordination Polymers Formed by Co(II) Diketonates with Pentaheterocyclic Triphenodioxazines

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Supplementary Materials:

1. X-ray data

Table S1. Bond lengths [Å] and angles [deg] for **IIc**

Co(1)-O(4)	2.033(2)	O(4)-Co(1)-N(1)	90.76(6)
Co(1)-O(3)	2.051(2)	O(3)-Co(1)-N(1)	94.39(7)
Co(1)-N(1)	2.357(2)	O(5)-Co(2)-O(6)	88.30(7)
Co(2)-O(5)	2.015(2)	O(5)-Co(2)-N(2)	92.37(6)
Co(2)-O(6)	2.023(2)	O(6)-Co(2)-N(2)	91.18(6)
Co(2)-N(2)	2.447(2)	C(1)-O(1)-C(7)	119.42(16)
Cl(1)-C(16)	1.737(2)	C(4)-O(2)-C(13)	118.20(16)
O(1)-C(1)	1.352(2)	C(27)-O(3)-Co(1)	127.57(14)
O(1)-C(7)	1.380(2)	C(29)-O(4)-Co(1)	128.19(15)
O(2)-C(4)	1.356(2)	C(32)-O(5)-Co(2)	126.27(14)
O(2)-C(13)	1.370(2)	C(34)-O(6)-Co(2)	126.17(14)
O(3)-C(27)	1.249(3)	C(2)-N(1)-C(8)	116.48(17)
O(4)-C(29)	1.249(3)	C(2)-N(1)-Co(1)	122.75(13)
O(5)-C(32)	1.256(3)	C(8)-N(1)-Co(1)	120.70(13)
O(6)-C(34)	1.252(3)	C(5)-N(2)-C(14)	115.48(17)
N(1)-C(2)	1.327(3)	C(5)-N(2)-Co(2)	123.91(13)
N(1)-C(8)	1.402(3)	C(14)-N(2)-Co(2)	120.35(13)
N(2)-C(5)	1.332(3)	O(1)-C(1)-C(6)	117.29(18)
N(2)-C(14)	1.411(3)	O(1)-C(1)-C(2)	118.96(17)
C(1)-C(6)	1.363(3)	C(6)-C(1)-C(2)	123.74(19)
C(1)-C(2)	1.457(3)	N(1)-C(2)-C(3)	122.06(18)
C(2)-C(3)	1.425(3)	N(1)-C(2)-C(1)	122.88(18)
C(3)-C(4)	1.352(3)	C(3)-C(2)-C(1)	115.06(18)
C(4)-C(5)	1.458(3)	C(4)-C(3)-C(2)	121.12(19)
C(5)-C(6)	1.427(3)	C(3)-C(4)-O(2)	115.92(18)
C(7)-C(12)	1.401(3)	C(3)-C(4)-C(5)	124.20(19)
C(7)-C(8)	1.402(3)	O(2)-C(4)-C(5)	119.87(18)
C(8)-C(9)	1.403(3)	N(2)-C(5)-C(6)	122.14(18)
C(9)-C(10)	1.382(3)	N(2)-C(5)-C(4)	123.03(18)
C(10)-C(11)	1.406(3)	C(6)-C(5)-C(4)	114.82(18)
C(10)-C(19)	1.534(3)	C(1)-C(6)-C(5)	121.01(19)
C(11)-C(12)	1.389(3)	O(1)-C(7)-C(12)	117.46(17)
C(12)-C(23)	1.536(3)	O(1)-C(7)-C(8)	119.74(18)
C(13)-C(18)	1.381(3)	C(12)-C(7)-C(8)	122.78(18)
C(13)-C(14)	1.398(3)	N(1)-C(8)-C(7)	122.10(18)
C(14)-C(15)	1.402(3)	N(1)-C(8)-C(9)	119.41(18)
C(15)-C(16)	1.384(3)	C(7)-C(8)-C(9)	118.36(19)
C(16)-C(17)	1.389(3)	C(10)-C(9)-C(8)	121.18(19)
C(17)-C(18)	1.383(3)	C(9)-C(10)-C(11)	117.93(19)
O(4)-Co(1)-O(3)	86.48(6)		

Table S2. Bond lengths [Å] and angles [deg] for **IIb**

Co(1)-O(3)	2.021(2)	O(5)-Co(2)-N(2)	90.69(7)
Co(1)-O(4)	2.035(2)		93.73(7)
Co(1)-N(1)	2.387(2)	O(6)-Co(2)-N(2)	127.14(17)
Co(2)-O(5)	2.022(2)		127.29(18)
Co(2)-O(6)	2.029(2)	C(32)-O(5)-Co(2)	115.8(2)
Co(2)-N(2)	2.363(2)		120.37(15)
O(5)-C(32)	1.259(3)		122.87(15)

O(6)-C(34)	1.255(3)	C(34)-O(6)-Co(2)	118.25(19)
N(2)-C(5)	1.324(3)	C(5)-N(2)-C(14)	119.07(18)
N(2)-C(14)	1.403(3)	C(5)-N(2)-Co(2)	127.15(19)
O(2)-C(4)	1.361(3)	C(14)-N(2)-Co(2)	127.1(2)
O(2)-C(13)	1.373(3)	C(4)-O(2)-C(13)	116.5(2)
O(1)-C(1)	1.350(3)	C(1)-O(1)-C(7)	122.03(16)
O(1)-C(7)	1.376(3)	C(29)-O(4)-Co(1)	121.27(15)
O(4)-C(29)	1.253(3)	C(27)-O(3)-Co(1)	117.1(2)
O(3)-C(27)	1.251(3)	C(2)-N(1)-C(8)	121.8(2)
N(1)-C(2)	1.325(3)	C(2)-N(1)-Co(1)	121.1(2)
N(1)-C(8)	1.407(3)	C(8)-N(1)-Co(1)	120.8(2)
C(14)-C(13)	1.397(3)	C(13)-C(14)-C(15)	120.6(2)
C(14)-C(15)	1.401(3)	C(13)-C(14)-N(2)	119.9(2)
C(15)-C(16)	1.378(4)	C(15)-C(14)-N(2)	119.0(2)
C(16)-C(17)	1.391(4)	C(16)-C(15)-C(14)	116.0(2)
C(17)-C(18)	1.380(4)	C(15)-C(16)-C(17)	121.5(2)
C(18)-C(13)	1.383(3)	C(18)-C(17)-C(16)	122.5(2)
C(4)-C(3)	1.353(3)	C(17)-C(18)-C(13)	117.3(2)
C(4)-C(5)	1.460(3)	O(2)-C(13)-C(18)	123.9(2)
C(3)-C(2)	1.425(3)	O(2)-C(13)-C(14)	118.8(2)
C(2)-C(1)	1.456(3)	C(18)-C(13)-C(14)	120.7(2)
C(8)-C(9)	1.399(3)	C(3)-C(4)-O(2)	122.5(2)
C(8)-C(7)	1.402(3)	C(3)-C(4)-C(5)	122.2(2)
C(9)-C(10)	1.380(4)	O(2)-C(4)-C(5)	115.3(2)
C(10)-C(11)	1.402(4)	C(4)-C(3)-C(2)	117.8(2)
C(1)-C(6)	1.355(3)	N(1)-C(2)-C(3)	119.8(2)
C(6)-C(5)	1.416(3)	N(1)-C(2)-C(1)	122.3(2)
O(3)-Co(1)-O(4)	87.63(8)	C(3)-C(2)-C(1)	121.0(2)
O(3)-Co(1)-N(1)	88.22(7)	C(9)-C(8)-C(7)	118.7(2)
O(4)-Co(1)-N(1)	85.98(8)	C(9)-C(8)-N(1)	
O(5)-Co(2)-O(6)	87.57(8)	C(7)-C(8)-N(1)	
		C(10)-C(9)-C(8)	
		C(9)-C(10)-C(11)	

Table S3. Bond lengths [Å] and angles [deg] for **IIa**

Co(1)-O(3)	1.994(3)	C(17)-C(16)-Cl(1)	118.73(17)
Co(1)-O(4)	1.997(3)	C(18)-C(17)-C(16)	118.4(2)
Co(1)-N(1)	2.674(3)	C(13)-C(18)-C(17)	119.4(2)
Cl(1)-C(16)	1.738(2)	O(2)-C(13)-C(18)	116.94(19)
O(1)-C(1)	1.364(2)	O(2)-C(13)-C(14)	120.79(19)
O(1)-C(7)	1.377(2)	C(18)-C(13)-C(14)	122.3(2)
O(2)-C(4)	1.369(2)	C(3)-C(4)-O(2)	117.66(18)
O(2)-C(13)	1.375(2)	C(3)-C(4)-C(5)	123.41(19)
O(3)-C(29)	1.267(5)	O(2)-C(4)-C(5)	118.92(18)
O(4)-C(27)	1.261(5)	C(4)-C(3)-C(2)	120.41(18)
N(1)-C(2)	1.311(3)	N(1)-C(2)-C(3)	121.06(17)
N(1)-C(8)	1.393(2)	N(1)-C(2)-C(1)	123.06(18)
N(2)-C(5)	1.316(3)	C(3)-C(2)-C(1)	115.88(18)
N(2)-C(14)	1.393(3)	C(8)-C(9)-C(10)	119.15(17)
C(4)-C(3)	1.349(3)	C(8)-C(7)-C(9)	122.22(18)
C(4)-C(5)	1.462(3)	C(8)-C(7)-O(1)	118.63(18)
C(3)-C(2)	1.435(3)	C(9)-C(7)-O(1)	121.19(18)
C(2)-C(1)	1.456(3)	C(7)-C(8)-C(9)	117.79(19)
C(8)-C(9)	1.396(3)	C(7)-C(8)-N(1)	120.82(17)
C(8)-C(7)	1.397(3)	C(9)-C(8)-N(1)	121.37(18)
C(9)-C(10)	1.391(3)	C(10)-C(9)-C(8)	108.6(2)
C(10)-C(11)	1.402(3)	C(9)-C(10)-C(11)	108.7(2)
C(10)-C(19)	1.540(3)	C(9)-C(10)-C(19)	108.01(18)
C(19)-C(20)	1.525(3)	C(11)-C(10)-C(19)	110.47(17)
C(19)-C(22)	1.527(3)	C(12)-C(11)-C(10)	112.67(17)
C(19)-C(21)	1.533(3)	C(11)-C(12)-C(7)	108.33(18)
C(11)-C(12)	1.395(3)	C(1)-C(6)-C(5)	123.48(19)
C(12)-C(7)	1.396(3)	C(4)-C(5)-C(6)	116.19(17)
C(1)-C(6)	1.346(3)	C(4)-C(5)-C(10)	122.50(18)
C(6)-C(5)	1.431(3)	C(6)-C(5)-C(10)	121.31(18)
O(3)-Co(1)-N(1)	63.91(9)	C(6)-C(1)-C(2)	111.52(18)
O(4)-Co(1)-N(1)	117.64(9)	C(6)-C(1)-O(1)	107.92(18)
	119.50(15)	C(2)-C(1)-O(1)	110.24(16)
	118.08(16)	C(1)-O(1)-C(7)	107.17(18)

C(1)-O(1)-C(7)	126.6(3)	C(9)-C(10)-	109.27(17)
C(4)-O(2)-	126.5(3)	C(11)	110.68(18)
C(13)	117.13(16)	C(9)-C(10)-	117.62(16)
C(29)-O(3)-	18.64(10)	C(19)	119.66(17)
Co(1)	98.50(11)	C(11)-C(10)-	122.71(18)
C(27)-O(4)-	116.02(18)	C(19)	117.71(17)
Co(1)	124.1(4)	C(20)-C(19)-	123.88(18)
C(2)-N(1)-C(8)	122.60(19)	C(22)	118.41(17)
C(2)-N(1)-	119.54(19)	C(20)-C(19)-	120.34(18)
Co(1)	117.9(2)	C(21)	120.36(19)
C(8)-N(1)-	119.4(2)	C(22)-C(19)-	123.57(19)
Co(1)	122.6(2)	C(21)	116.07(18)
C(5)-N(2)-	118.66(18)	C(20)-C(19)-	
C(14)		C(10)	
O(3)-C(29)-		C(22)-C(19)-	
C(28)		C(10)	
N(2)-C(14)-		C(21)-C(19)-	
C(13)		C(10)	
N(2)-C(14)-		C(12)-C(11)-	
C(15)		C(10)	
C(13)-C(14)-		C(11)-C(12)-	
C(15)		C(7)	
C(16)-C(15)-		C(11)-C(12)-	
C(14)		C(23)	
C(15)-C(16)-		C(7)-C(12)-	
C(17)		C(23)	
C(15)-C(16)-		C(25)-C(23)-	
Cl(1)		C(12)	
		C(25)-C(23)-	
		C(26)	
		C(12)-C(23)-	
		C(26)	
		C(25)-C(23)-	
		C(24)	
		C(12)-C(23)-	
		C(24)	
		C(26)-C(23)-	
		C(24)	
		O(1)-C(7)-	
		C(12)	
		O(1)-C(7)-	
		C(8)	
		C(12)-C(7)-	
		C(8)	
		C(6)-C(1)-	
		O(1)	
		C(6)-C(1)-	
		C(2)	
		O(1)-C(1)-	
		C(2)	
		C(1)-C(6)-	
		C(5)	
		N(2)-C(5)-	
		C(6)	
		N(2)-C(5)-	
		C(4)	
		C(6)-C(5)-	
		C(4)	

Table S4. Bond lengths [Å] and angles [deg] for **I**

Cl(1)-C(16)	1.747(3)	C(10)-C(9)-	120.9(3)
O(1)-C(1)	1.364(3)	C(8)	118.3(3)
O(1)-C(7)	1.391(3)	C(9)-C(10)-	122.7(3)
O(2)-C(4)	1.370(3)	C(11)	119.0(3)
O(2)-C(13)	1.383(3)	C(9)-C(10)-	123.8(3)
N(1)-C(2)	1.313(4)	C(19)	115.4(3)
N(1)-C(8)	1.397(3)	C(11)-C(10)-	122.6(3)
N(2)-C(5)	1.314(4)	C(19)	122.0(3)
N(2)-C(14)	1.398(4)	C(12)-C(11)-	118.8(2)
C(9)-C(10)	1.376(4)	C(10)	118.1(3)
C(9)-C(8)	1.409(4)	C(7)-C(12)-	123.1(3)
C(10)-C(11)	1.406(4)	C(11)	123.2(3)
C(10)-C(19)	1.546(4)	C(7)-C(12)-	118.2(3)
C(11)-C(12)	1.403(4)	C(23)	118.6(3)
C(12)-C(7)	1.400(4)	C(11)-C(12)-	118.7(3)
C(12)-C(23)	1.539(4)	C(23)	122.8(3)
C(7)-C(8)	1.399(4)	O(1)-C(7)-C(8)	118.6(2)
C(1)-C(6)	1.353(4)	O(1)-C(7)-	120.0(3)
C(1)-C(2)	1.457(4)	C(12)	123.4(3)
C(2)-C(3)	1.437(4)	C(8)-C(7)-	116.6(3)
C(3)-C(4)	1.351(4)	C(12)	120.7(3)
C(4)-C(5)	1.464(4)	N(1)-C(8)-C(7)	118.4(3)
C(5)-C(6)	1.435(4)	N(1)-C(8)-C(9)	122.7(3)
C(13)-C(18)	1.386(4)	C(7)-C(8)-C(9)	119.0(2)

C(13)-C(14)	1.400(4)	C(6)-C(1)-O(1)	120.3(3)
C(14)-C(15)	1.408(4)	C(6)-C(1)-C(2)	123.3(3)
C(15)-C(16)	1.377(4)	O(1)-C(1)-C(2)	116.4(3)
C(16)-C(17)	1.398(4)	N(1)-C(2)-C(3)	120.8(3)
C(17)-C(18)	1.391(4)	N(1)-C(2)-C(1)	117.6(3)
C(19)-C(21)	1.527(4)	C(3)-C(2)-C(1)	120.2(2)
C(19)-C(20)	1.533(4)	C(4)-C(3)-C(2)	122.2(3)
C(19)-C(22)	1.544(4)	C(3)-C(4)-O(2)	122.7(3)
C(1)-O(1)-C(7)	119.4(2)	C(3)-C(4)-C(5)	119.5(3)
C(4)-O(2)-C(13)	118.3(2)	O(2)-C(4)-C(5)	117.8(3)
C(2)-N(1)-C(8)	116.4(2)	N(2)-C(5)-C(6)	119.7(3)
C(5)-N(2)-C(14)	116.3(3)	N(2)-C(5)-C(4)	122.2(3)
		C(6)-C(5)-C(4)	119.2(2)
		C(1)-C(6)-C(5)	118.7(2)
		O(2)-C(13)-C(18)	118.6(3)
		O(2)-C(13)-C(14)	
		C(18)-C(13)-C(14)	
		N(2)-C(14)-C(13)	
		N(2)-C(14)-C(15)	
		C(13)-C(14)-C(15)	
		C(16)-C(15)-C(14)	
		C(15)-C(16)-C(17)	
		C(15)-C(16)-Cl(1)	
		C(17)-C(16)-Cl(1)	
		C(18)-C(17)-C(16)	

2. XPS investigations

Techniques

The elemental analysis of the surface layers of the **IIa** sample was performed on an X-ray photoelectron spectrophotometer SPECS PHOIBOS 150 MCD (E MgK_{α} = 1253.6 eV). Residual pressure in the working chamber did not exceed 10^{-10} Torr. An analysis area of the sample was ≈ 300 x 700 μm². The average depth of XPS analysis was ≈ 2-5 nm. Accuracy of the chemical state and binding energies (E_B) for core-levels of main elements determination was 0.1 eV. A thick layer of the sample was deposited on the surface of the double-sided adhesion carbon tape to exclude appearance of the substrate material lines in the spectra. XPS spectra have been measured at room temperature. Approximation of the spectra was done as a sum of Lorentzian (30%) and Gaussian (70 %) functions. The decomposition was carried out after subtracting the background according to the Shirley method [2S1]. The spectra were recorded in the constant transmission energy mode of 40 eV for the survey spectrum and 10 eV for the lines of the Cl(2p), C(1s), N(1s), O(1s), Co(2p) levels. XPS spectra were analyzed using the CasaXPS 2.3.23 software [2S2].

Results

Survey XPS spectrum of the **IIa** sample was carried out in an energy range of 0 – 1000 eV (Figure A1). These spectra contain the lines corresponding to electronic transitions in the core electron shells of the Cl(2p), C(1s), N(1s), O(1s), and Co(2p) levels. The arrows show Auger transitions of oxygen (O KLL) and cobalt (Co LMM). The line positions of the corresponding elements and relative concentration of the main elements are shown in Table 1. Content of the elements in the near-surface layer: oxygen (11.1 At., %), carbon (80.5 At., %), nitrogen (3.21 At., %), cobalt (1.89 At., %), and chlorine (3.3 At., %). Ratio of Co to Cl concentrations is close to 1:2 (see Table 2S1).

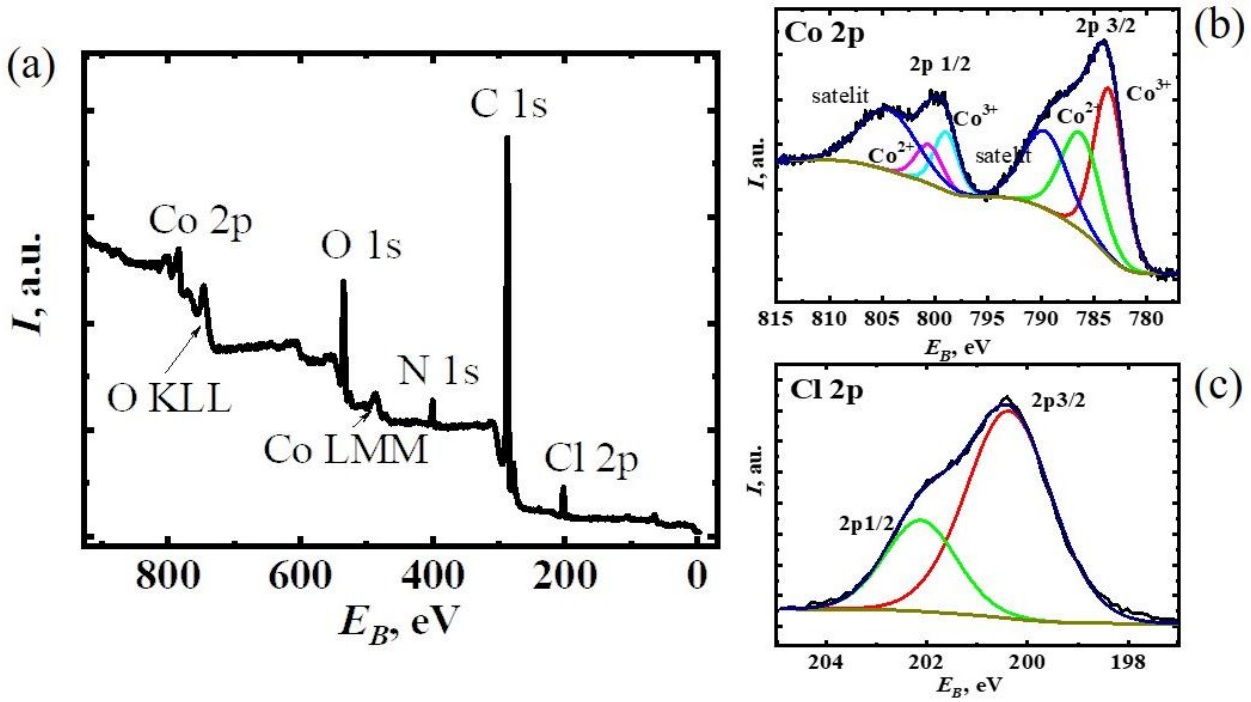

Figure 2S1. XPS of IIa: survey spectrum (a), spectrum of Co 2p line (b). spectrum of Cl 2p line (c)

Table 2S1. Main characteristics of Cl (2p), C(1s), N(1s), O(1s), Co(2p) lines

#	**Name**	Position, eV	FWHW, eV	Area	**At., %**
1	**O 1s**	535	3.56	9879	**11.1**
2	**C 1s**	287	2.93	24960	**80.5**
3	**N 1s**	400	2.45	1764	**3.21**
4	**Co 2p**	784	6.62	10863	**1.89**
5	**Cl 2p**	202	3.16	2350	**3.3**

The presence of several types of the carbon bonds in the **IIa** samples is confirmed by deconvolution of the C 1s and O 1s spectra (Figure 2S2 a, b). Spectrum of the C 1s level was decomposed into six possible components with the bond energies 285 eV (C-C), 284.24 eV (C-H), 285.91 eV (C-N), 286.54 eV (C-OH), and 287.81 eV (C-Cl) (Figure 2S2a). The presence of the OH hydroxyl groups is detected in the spectrum of the O 1s line, too (Figure 2S2b). Deconvolution of the peak into three components detects the maxima with the binding energies at 531.26 eV, 532.82 eV, and 533.89 eV, which correspond to the oxygen bonds with the carbon, hydroxyl groups, and cobalt, respectively.

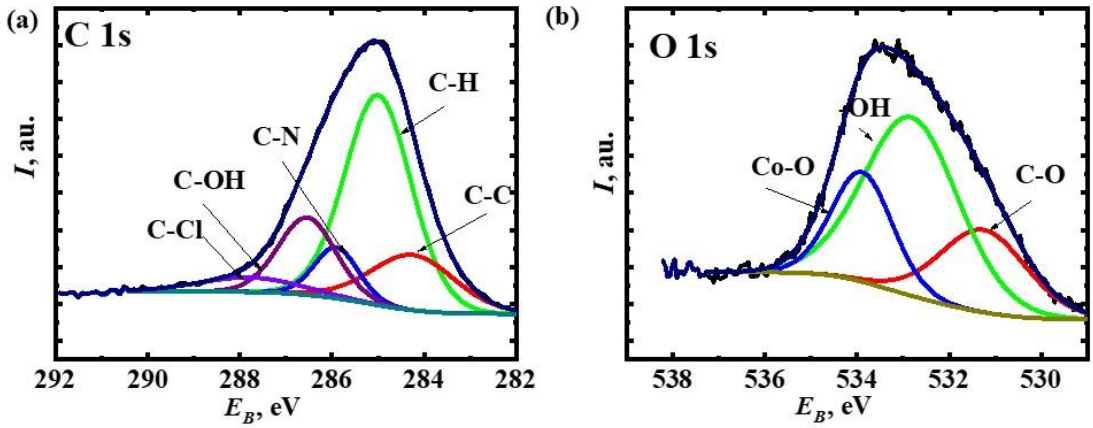

Figure 2S2. High resolution XPS spectrum: C 1s level (a)and O 1s level (b)

S 1. Shirley, D.A. High-resolution X-ray photoelectron spectrum of the valence band of gold. *Phys. Rev. B*, 1972, *5*, N 5, 4702-4714. https://doi.org/10.1103/PhysRevB.5.4709.
S 2. http://www.casaxps.com/

3. **Magnetic data**

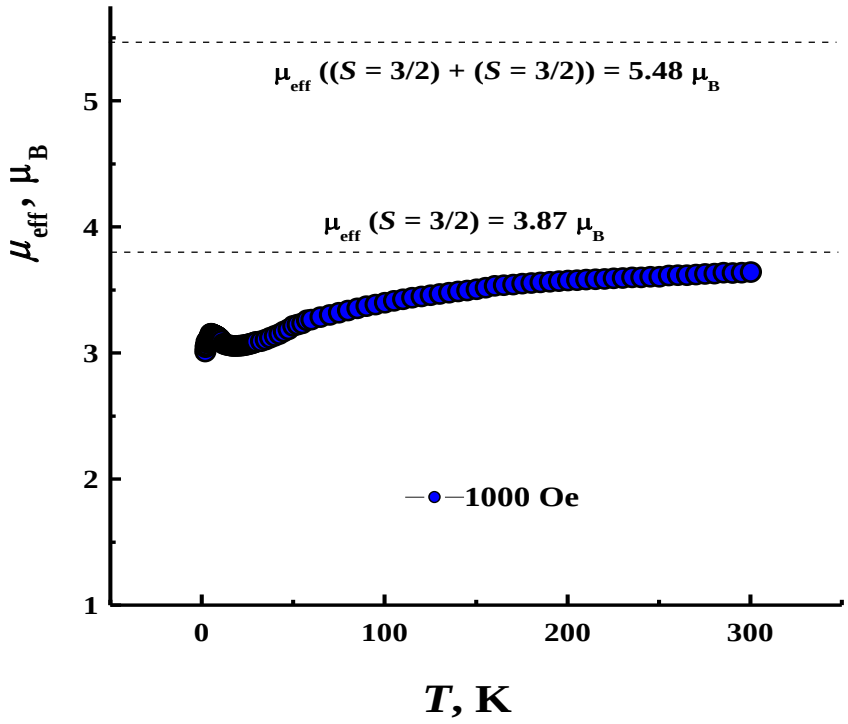

Figure 3S1. Dependence of the effective magnetic moment on temperature before extraction of the ferromagnetic contribution in sample IIa.