Electronic Supplementary Material (ESI) for New Journal of Chemistry.

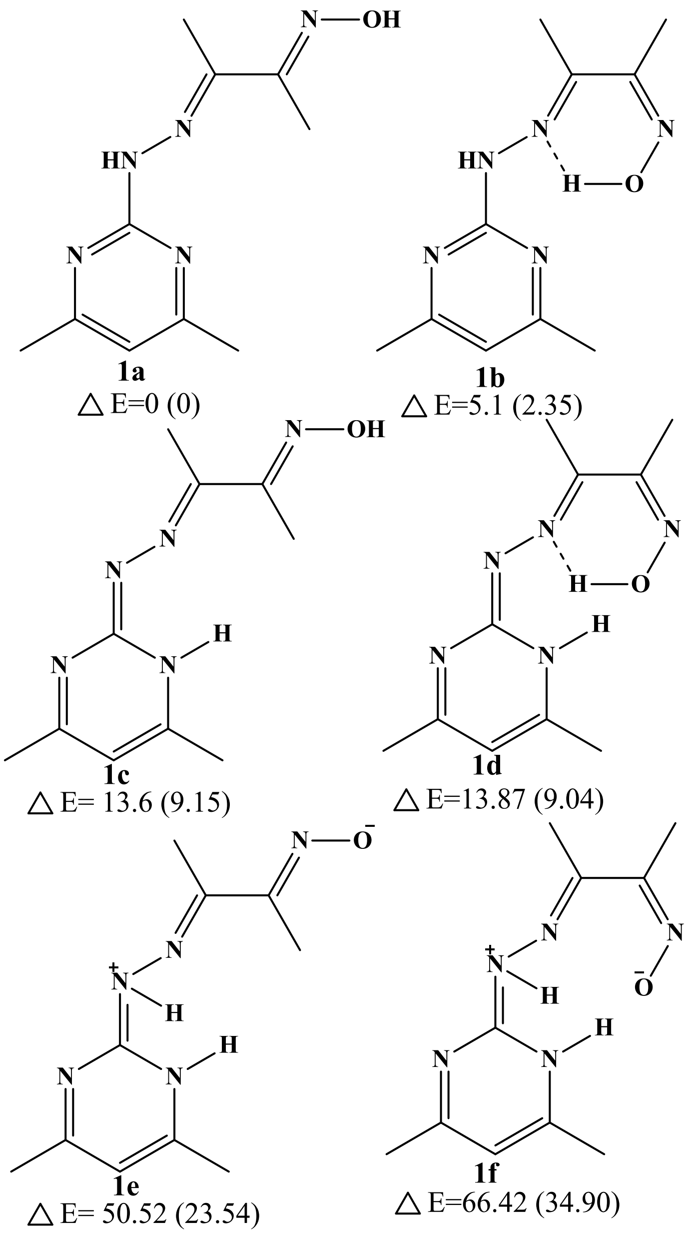
Electronic supplementary information

Theoretical and experimental study of the coordination ability of 4,6-dimethylpyrimidinylhydrazone diacetylmonooxime towards Ni(II), Mn(II), Fe(III) and Co(III) ions

Vladimir V. Lukov [a], Arshak A. Tsaturyan [b]*, Yulia P. Tupolova [a],
Leonid D. Popov [a], Igor N. Shcherbakov [a] Vladimir E. Lebedev [a],
Olga I. Askalepova [a], Tatiana A. Lastovina [c], Vladimir A. Lazarenko [d],
Victor N. Khustalev [e], Jordan C. Poler [f]

[a] *Department of Chemistry, Southern Federal University, 7, Zorge Str., Rostov-on-Don, 344090 Russia*
[b] *Institute of Physical and Organic Chemistry, Southern Federal University, Stachki Av. 194/2 Rostov-on-Don, 344090 Russia*
[c] *Southern Scientific Center, Russian Academy of Sciences, 41 Chehova str, Rostov-on-Don, 344006 Russia*
[d] *National Research Center "Kurchatov Institute", Acad. Kurchatov Sq., 1, Moscow, 123182, Russia*
[e] *Inorganic Chemistry Department, Peoples' Friendship University of Russia, 6 Miklukho-Maklay St., Moscow, 117198, Russia*
[f] *Department of Chemistry, University of North Carolina at Charlotte, 28223 Charlotte, NC, USA*

***Corresponding author: caturyan@sfedu.ru (TAA)**



1a
△ E=0 (0)

1b
△ E=5.1 (2.35)

1c
△ E= 13.6 (9.15)

1d
△ E=13.87 (9.04)

1e
△ E= 50.52 (23.54)

1f
△ E=66.42 (34.90)

Figure S1. Sketch of the of the tautomeric form of the hetarilhydrazone **1** and the relative stability energies (kcal/mol) in gas phase and water medium (value in brackets) obtained for optimized structures at B3LYP/6–311++G(d,p) level of theory.

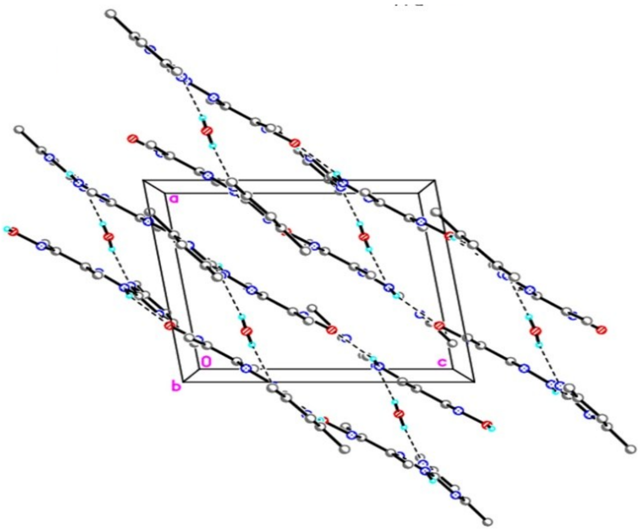


Figure S2. Crystal structure of $\mathbf{H_2L}$ • ½H_2O along the crystallographic ***b*** axis.

Table S1. Structural characteristics of the HBs in the crystals of $\mathbf{H_2L}$ • ½H_2O

HB	D – H, Å	H...A, Å	D...A, Å	D - H...A, deg
O1─H1O···N5^{i}	0.84(2)	1.89(2)	2.723(1)	168(2)
O2─H2O···N4^{ii}	0.88(2)	2.21(2)	2.970(1)	145(2)
N3─H3N···O1^{iii}	0.90(2)	2.49(2)	3.238(1)	141(2)

(symmetry codes: (i) *x*-1/2, -*y*+1, *z*+1/2; (ii) *x*+1/2, -*y*+1, *z*+1/2; (iii) *x*+1/2, -*y*+1, *z*-1/2)

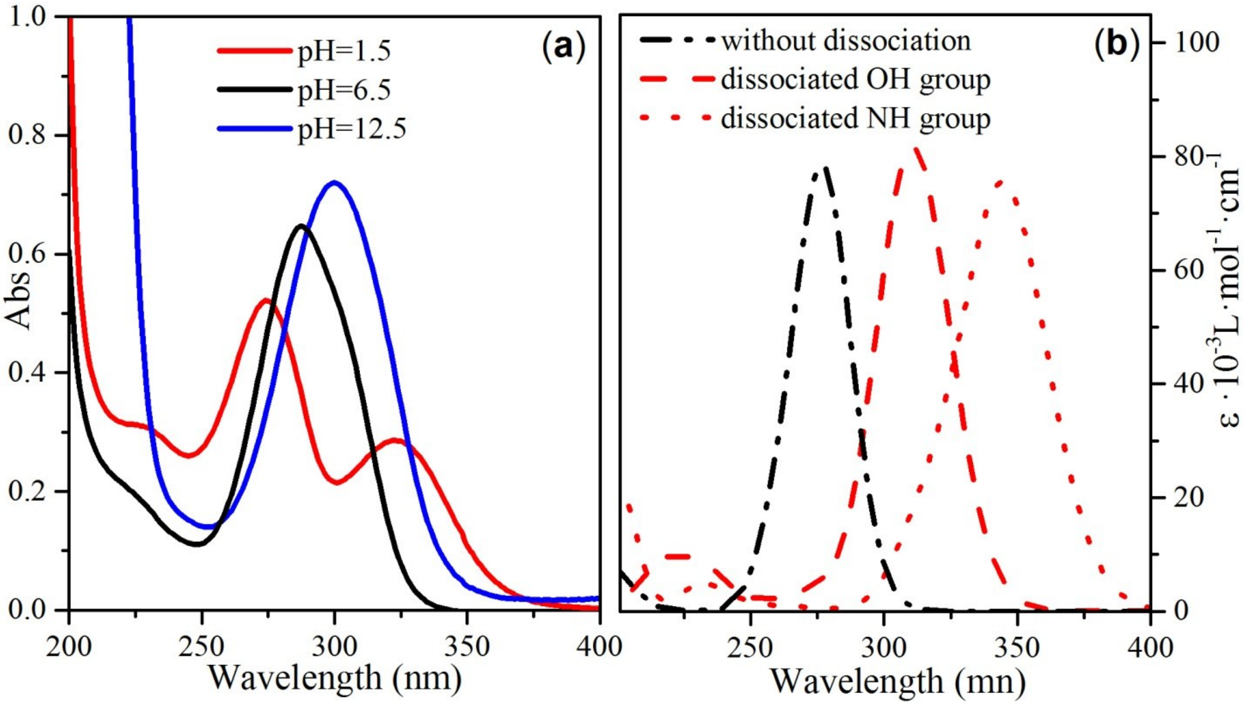


Figure S3. Experimental (panel a) and simulated (panel b) electronic absorption spectra of hetarylhydrazone **1** at various pH in H_2O:EtOH (1:1) medium, C = 1.95 10^{-5} M Experimental UV spectra shown for the ligand solution set to pH=1.5 - red line, pH=6.5 - yellow line, and pH=12.5 -blue line. Simulated spectra by using TD-CAMB3LYP/6-311++G(d,p) level of theory with accounting ethanol medium for neutral from of hetarilhydrazone **1** – black dash dot line, dissociated form through OH group - red dash line and through NH group - red dash line.

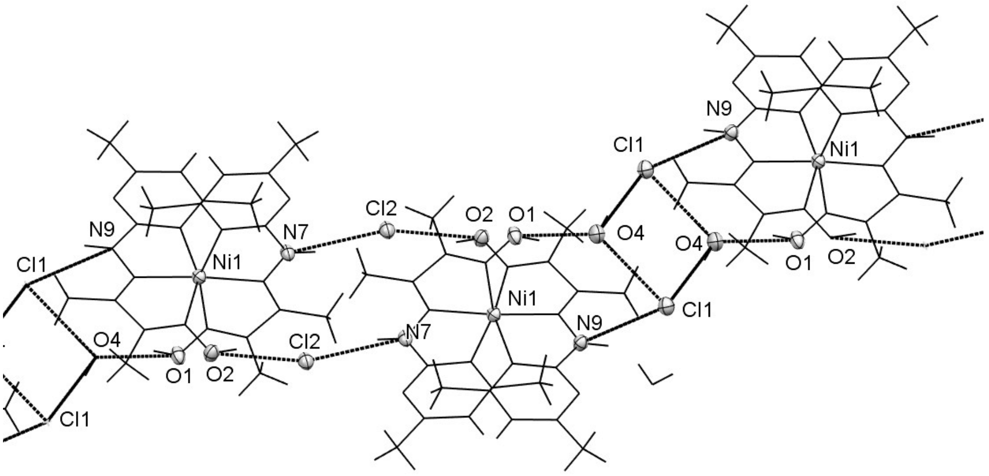


Figure 4. Fragment of the infinite HB chain in crystals of **2a**.

Table S2. Structural characteristics of the HBs in the crystals of **2a**

HB	D – H, Å	H...A, Å	D...A, Å	D - H...A, deg
O2–H2…Cl2	0.82	2.16	2.9322(19)	157
N7–H7…Cl2$^{(i)}$	0.86	2.34	3.181(2)	164
O1–H1…O4	0.82	1.79	2.570(3)	158
O4–H4A…Cl1$^{(ii)}$	0.85	2.30	3.143(2)	172
O4–H4B…Cl1	0.85	2.26	3.112(2)	177
N9–H9…Cl1	0.86	2.56	3.158(2)	128

(symmetry codes: (i) 1-x,1-y,1-z; (ii) 1-x, 2-y, 2-z)

Table S3. Comparison of the selected bond lengths (Å) in compounds **2a**, **2c** and **3** from single crystal diffraction experiment.

Bond	**2a** (M=Ni)		**2c** (M=Mn)[a]	**3** (M=Co)	
$M\text{-}N_{hydr}$	Ni-N1	1.995(2)	2.210(2) ÷ 2.219(2)	Co1-N3	1.869(3)
	Ni-N2	2.001(2)			
$M\text{-}N_{ox}$	Ni1–N3	2.1193(18)	2.295(2) ÷ 2.304(2)	Co1-N10	1.914(3)
	Ni1–N4	2.147(2)			
$M\text{-}N_{pyr}$	Ni1–N1	2.174(2)	2.206(2) ÷ 2.286(2)	Co1–N2	2.031(3)
	Ni1–N6	2.1340(17)		Co1-N4	2.006(3)

[a] Statistic over two independent molecules in unit cell.

Table S4. Structural characteristics of the HBs in the crystals of **3**

HB	D – H, Å	H...A, Å	D...A, Å	D - H...A, deg
N7–H7…O3	0.86	2.10	2.951(4)	168
N7–H7…O4	0.86	2.57	3.203(4)	132
N9–H9…O1$^{(iii)}$	0.86	1.80	2.651(4)	170

O1…H9–N9$^{(iv)}$	0.86	1.80	2.651(4)	170

(symmetry codes: (iii) 1/2+x, y, 3/2-z; (iv) -1/2+x, y, 3/2-z)

Calculation details for pKa

The dissociation through an acidic mechanism can be represented as follows:

$$H_4L^{2+} \rightleftharpoons H_3L^+ + H^+ \quad pKa_1$$

$$H_3L^+ \rightleftharpoons H_2L + H^+ \quad pKa_2$$

$$H_2L \rightleftharpoons HL^- + H^+ \quad pKa_3$$

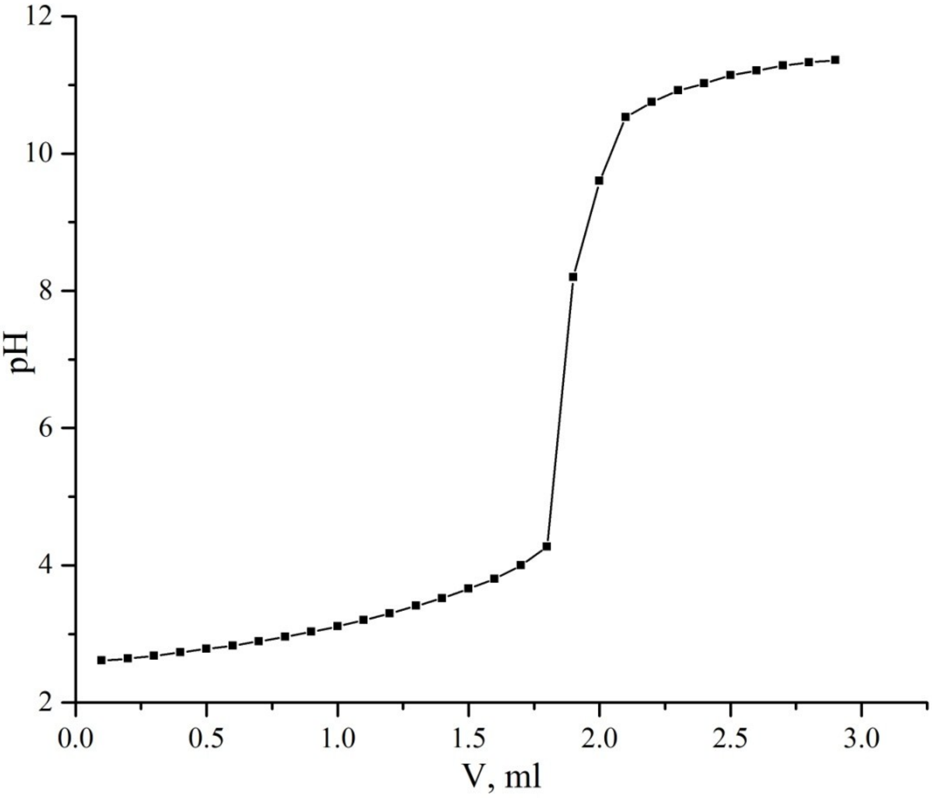


Figure S5. The titration curve of hetarylhydrazone **1**.

During the potentiometric measurements it was established that hetarylhydrazone under study revealed two protonation centers with close pKa values (ΔpKa<2,8) in the whole pH range. Therefore in order to calculate the pKa value the function of mean-value proton number has been used. [1]

$$n = \frac{(2 - a)C_R - [H^+] + [OH^-]}{C_R} \qquad (1)$$

where a is neutralization degree, C_R-molar concentration of substance under study.

Under potentiometric titration of acid or protonated base by alkaline solution, one can obtain the set of corresponding values of hydrogen ion's free concentrations and mean-value proton n numbers connected between each other by the equation (2):

$$n = \frac{(1-n)\cdot 10^{-pH}}{K_2} + \frac{(2-n)\cdot 10^{-2pH}}{K_1 K_2} \quad , \quad (2)$$

where K_1 and K_2 are the dissociation constants of acid associated with ionic or non-ionic base for the first and second stage correspondingly.

The equation (2) can be represented as a linear dependence:

$$\frac{n}{(1-n)[H^+]} = \frac{1}{K_2} + \frac{1}{K_1 K_2} \cdot \frac{(2-n)[H^+]}{(1-n)} \qquad (3)$$

where $\frac{n}{(1-n)[H^+]} = y$; $\frac{(2-n)[H^+]}{(1-n)} = x$

The pK_{a1}=2.39; pK_{a2}=3.26 values have been obtained by the least-squares method.

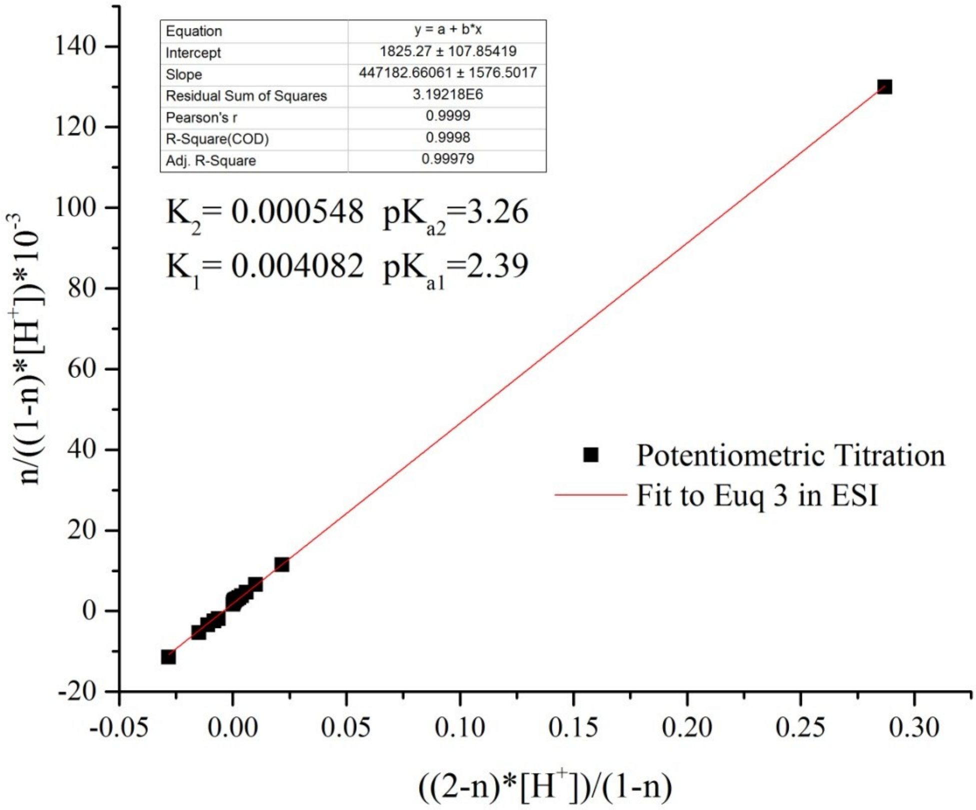


Figure S6. Fitting of experimental potentiometric titration data to equation 3 for hetarylhydrazone **1**

The data for protolithic equilibrium constant calculations are shown in Table S1

Table S5. The data for protolithic equilibrium constant calculations (pK_{a1}, pK_{a2}) in the pH range of 2.61 – 4.27

V	pH	a	$[H^+]$	$[OH^-]$	n	y	x
0.1	2.61	0.1059	2.45E-03	4.07E-12	1.28	-1.86E+03	-6.30E-03

0.2	2.64	0.2118	2.29E-03	4.37E-12	1.22	-2.46E+03	-8.34E-03
0.3	2.68	0.3177	2.09E-03	4.79E-12	1.16	-3.47E+03	-1.10E-02
0.4	2.73	0.4236	1.86E-03	5.37E-12	1.11	-5.38E+03	-1.49E-02
0.5	2.78	0.5295	1.66E-03	6.03E-12	1.06	-1.14E+04	-2.82E-02
0.6	2.83	0.6354	1.48E-03	6.76E-12	0.99	1.30E+05	2.87E-01
0.7	2.89	0.7413	1.29E-03	7.76E-12	0.94	1.15E+04	2.16E-02
0.8	2.96	0.8472	1.10E-03	9.12E-12	0.88	6.61E+03	1.01E-02
0.9	3.03	0.9531	9.33E-04	1.07E-11	0.81	4.68E+03	5.94E-03
1.0	3.11	1.0590	7.76E-04	1.29E-11	0.75	3.80E+03	3.84E-03
1.1	3.20	1.1649	6.31E-04	1.58E-11	0.68	3.33E+03	2.59E-03
1.2	3.30	1.2708	5.01E-04	2.00E-11	0.60	3.04E+03	1.77E-03
1.3	3.41	1.3767	3.89E-04	2.57E-11	0.53	2.85E+03	1.21E-03
1.4	3.52	1.4826	3.02E-04	3.31E-11	0.44	2.62E+03	8.43E-04
1.5	3.66	1.5885	2.19E-04	4.57E-11	0.36	2.54E+03	5.59E-04
1.6	3.80	1.6944	1.58E-04	6.31E-11	0.27	2.29E+03	3.74E-04
1.7	4.00	1.8003	1.00E-04	1.00E-10	0.17	2.12E+03	2.21E-04
1.8	4.27	1.9062	5.37E-05	1.86E-10	0.08	1.63E+03	1.12E-04

The calculation of pK_{a3} was done by using following equation:

$$pK_a = pH + \lg\frac{(1-a)C_R - [H^+] + [OH^-]}{aC_R + [H^+] - [OH^-]} \qquad (4)$$

Where a is neutralization degree, C_R-molar concentration of substance under study

In the case of pH >5, the value of $[H^+]$ can be neglected.

Table S6. The data for protolithic equilibrium constant calculations (pK_{a3}) in the pH range of 10.53 – 11.36

V_{sum}	V for pK calcualtion	pH	a	$[H^+]$	$[OH^-]$	pK
2.1	0.1	10.53	0.1015	2.95E-11	0.000339	12.29762
2.2	0.2	10.75	0.203	1.78E-11	0.000562	11.92672
2.3	0.3	10.92	0.3045	1.2E-11	0.000832	11.89111

2.4	0.4	11.02	0.406	9.55E-12	0.001047	11.79334
2.5	0.5	11.14	0.5075	7.24E-12	0.00138	11.85244
2.6	0.6	11.21	0.609	6.17E-12	0.001622	11.80249
2.7	0.7	11.28	0.7105	5.25E-12	0.001905	11.79469
2.8	0.8	11.33	0.812	4.68E-12	0.002138	11.74555
2.9	0.9	11.36	0.9135	4.37E-12	0.002291	11.64655

It is difficult and challenging to accurately predict the pKa values of polyprotic compounds. There are only a few reports in the literature where theoretical calculations of pKa values accurately predicted experimental measurements of polyprotic compounds.[2-5] Also, the task becomes more difficult while attempting to predict the pKa for OH or NH groups because these groups have such low acidity.[6]

The theoretical values of pKa were calculated by using thermodynamic cycle

$$\begin{tikzcd}
HR_{gas} \arrow[r, "\Delta G^0_{gas}"] \arrow[d, "\Delta G^*_{solv}(HR)"'] & R^-_{gas} \; + \arrow[d, "\Delta G^*_{solv}(R^-)"] & H^+_{gas} \arrow[d, "\Delta G^*_{solv}(H^+)"] \\
HR_{aq} \arrow[r, "\Delta G^*_{aq}"'] & R^-_{aq} \; + & H^+_{aq}
\end{tikzcd}$$

The equilibrium constant of the studies reaction may be calculated as:

$$K_a = \frac{[R^-][H^+]}{[HR]} \qquad (5)$$

$$pK_a = -\log_{10} K_a \qquad (6)$$

pKa value can be calculated from the Gibbs energy in the solution for the acid dissociation reaction:

$$pK_a = \frac{\Delta G^*_{aq}}{2.303RT} \qquad (7)$$

Here ΔG^*_{aq} is the Gibbs free energy of dissociation for HR can be defined as:

$$\Delta G^*_{aq} = G^*_{aq}(H^+) + G^*_{aq}(R^-) - G^*_{aq}(HR) \qquad (8)$$

where * denotes the standard state condition in 1 M solution at 298.25 K.

$$2.303RTpK_a = \Delta G^*_{aq} = \Delta G^0_{gas} + \Delta\Delta G^*_{solv} + \Delta G^{0\to *} \qquad (9)$$

Where ΔG^0_{gas} and $\Delta\Delta G^*_{solv}$ are given as:

$$\Delta G^0_{gas} = G^0_{gas}(R^-) + G^0_{gas}(H^+) - G^0_{gas}(HR) \qquad (10)$$

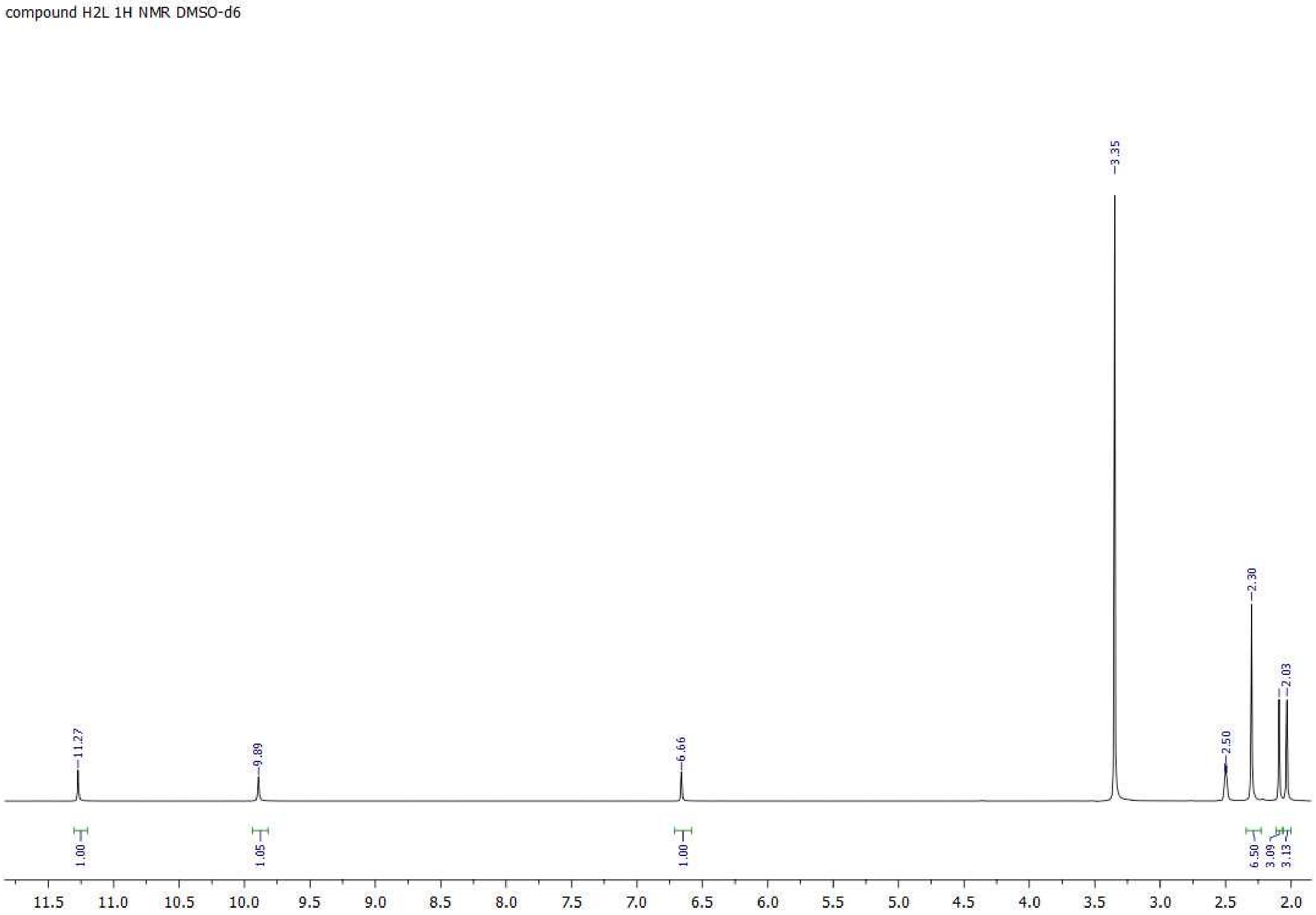
$$\Delta\Delta G^*_{solv} = \Delta G^*_{solv}(R^-) + \Delta G^*_{solv}(H^+) - \Delta G^*_{solv}(HR) \qquad (11)$$

The value of $\Delta G^0_{solv}(H^+)$ was under debate in the literature for some time. Nevertheless, the most reliable value of $\Delta G^0_{solv}(H^+)$ is generally accepted as -265.9 kcal/mol.[7] For a proton in the gas phase, the experimentally determined $\Delta G^0_{gas}(H^+)$ of -6.28 kcal/mol was used in the calculation.[8] The factor $\Delta G^{0\rightarrow *}$ accounting for the conversion between standard states of 1 atm and 1 mol/L was incorporated as RTln(24.46).

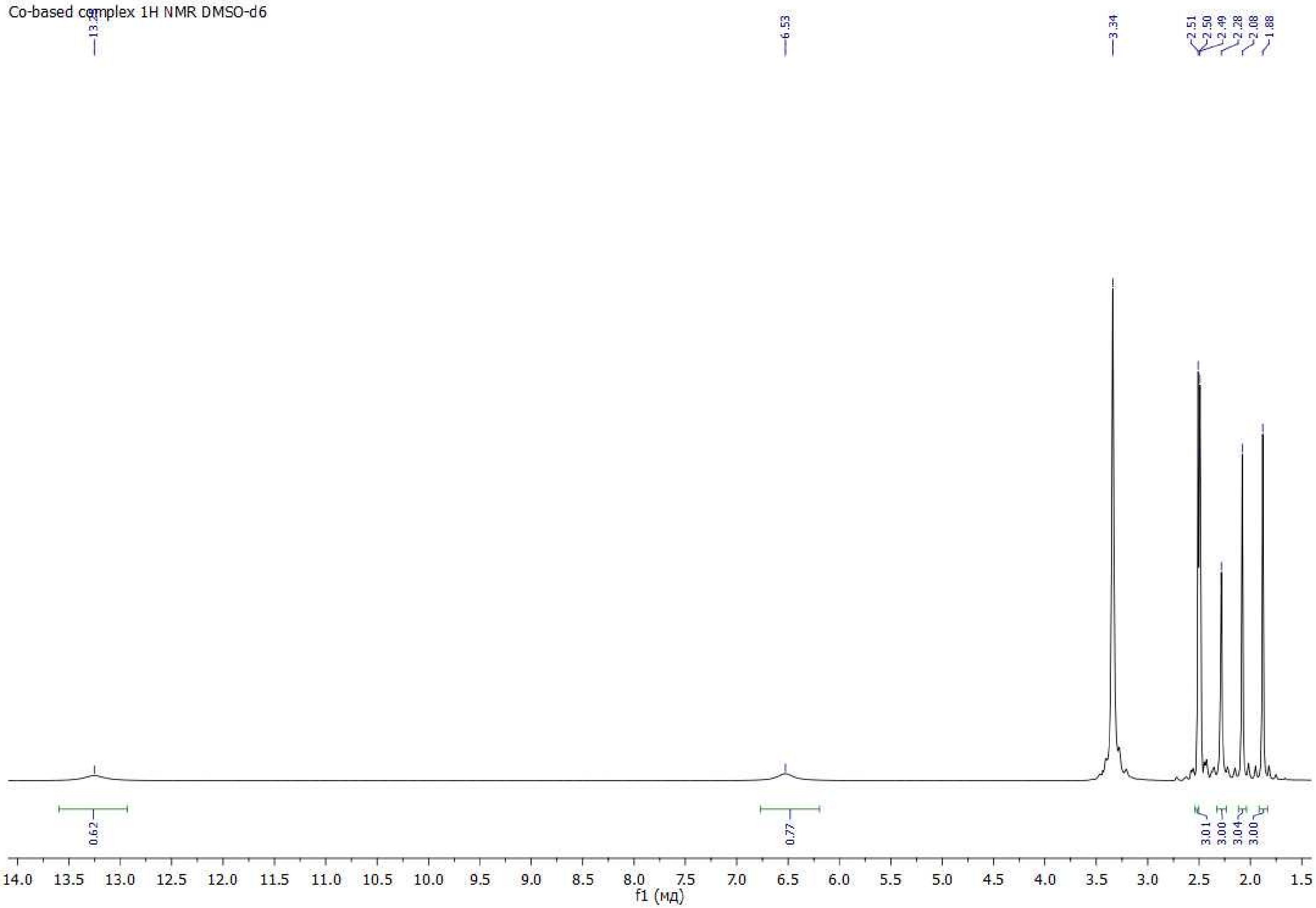
Table S7. Crystallographic data and details of the crystallographic experiment and refinement procedure.

Compound	**H_2L • ½H_2O**	**2a**	**2c**	**3**
Empirical formula	$C_{10}H_{16}N_5O_{1.5}$	$C_{20}H_{32}Cl_2N_{10}NiO_3$	$C_{20}H_{30.5}Cl_2MnN_{10}O_{10.25}$	$C_{20}H_{28}ClCoN_{10}O_6$
Formula weight	230.28	593.23	709.89	598.90
λ, Å	0.71073	0.7927	0.7927	0.8042
T, K	120(2)	100(2)	100(2)	293(2)
Crystal size, mm	0.32×0.20×0.20	0.03×0.03×0.05	0.04×0.04×0.06	0.03×0.03×0.15
Crystal system	Monoclinic	Triclinic	Triclinic	Orthorhombic
Space group	*P*2/n	P -1	P -1	Pbca
a, Å	10.0278(4)	11.070(2)	12.890(3)	8.1014(16)
b, Å	10.8150(4)	11.180(2)	15.010(3)	22.215(4)
c, Å	11.2650(4)	12.880(3)	15.150(3)	28.766(6)
α, °	90	70.07(3)	94.90(3)	90
β, °	98.834(1)	65.63(3)	91.49(3)	90
γ, °	90	88.17(3)	96.56(3)	90
V, Å^3	1207.20(8)	1354.0(6)	2899.5(11)	5177.1(18)
Z	4	2	4	8
D_{calc}, g·cm^{-3}	1.267	1.455	1.626	1.537
F(000)	492	592	1466	2480
μ, mm^{-1}	0.090	1.287	0.966	1.158
θ_{min}; θ_{max}, °	31.064	2.2; 28.2	1.5; 31.0	1.6; 31.0
Index ranges	-14 < h < 14 -15 < k < 15 -16 < l < 16	-12 < h < 13 -13 < k < 13 -14 < l < 15	-16 < h < 16 -18 < k < 19 -19 < l < 19	-9 < h < 10 -28 < k < 28 -36 < l < 36
Reflections collected	15468	16940	28426	52698
Independent reflections, R_{int}	3873, 0.042	4703, 0.0268	13037, 0.043	5568, 0.0453
Reflections observed with $I > 2\sigma(I)$	2661	4282	11068	4836
Data / restraints / parameters	3873 / 0 / 214	4703 / 0 / 353	13037 / 6 / 852	5568 / 0 / 352

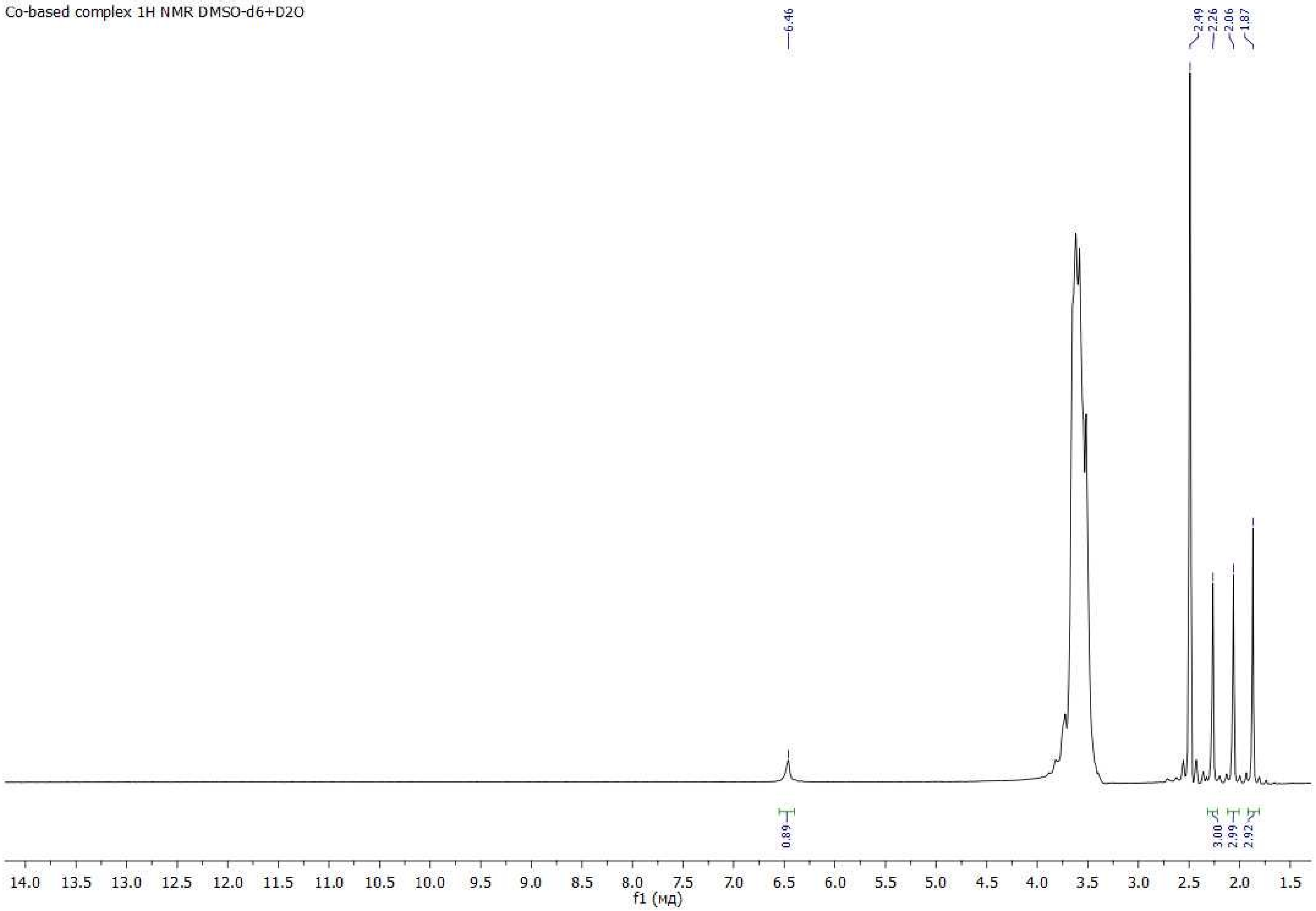
R_1; wR_2 ($I > 2\sigma(I)$)	0.046; 0.122	0.0325;0.0821	0.0487; 0.1290	0.0578; 0.1300
R_1; wR_2 [all data]	0.077; 0.139	0.0363;0.0844	0.0573; 0.1359	0.0662; 0.1346
GOF on F^2	1.023	1.038	1.042	1.142



FigureS7. ^{1}H-NMR spectrum of hetarylhydrazone **1**.



FigureS8. ^{1}H-NMR spectrum of complex **3** in DMSO



FigureS9. ^{1}H-NMR spectrum of complex **3** in DMSO with adding of D_2O

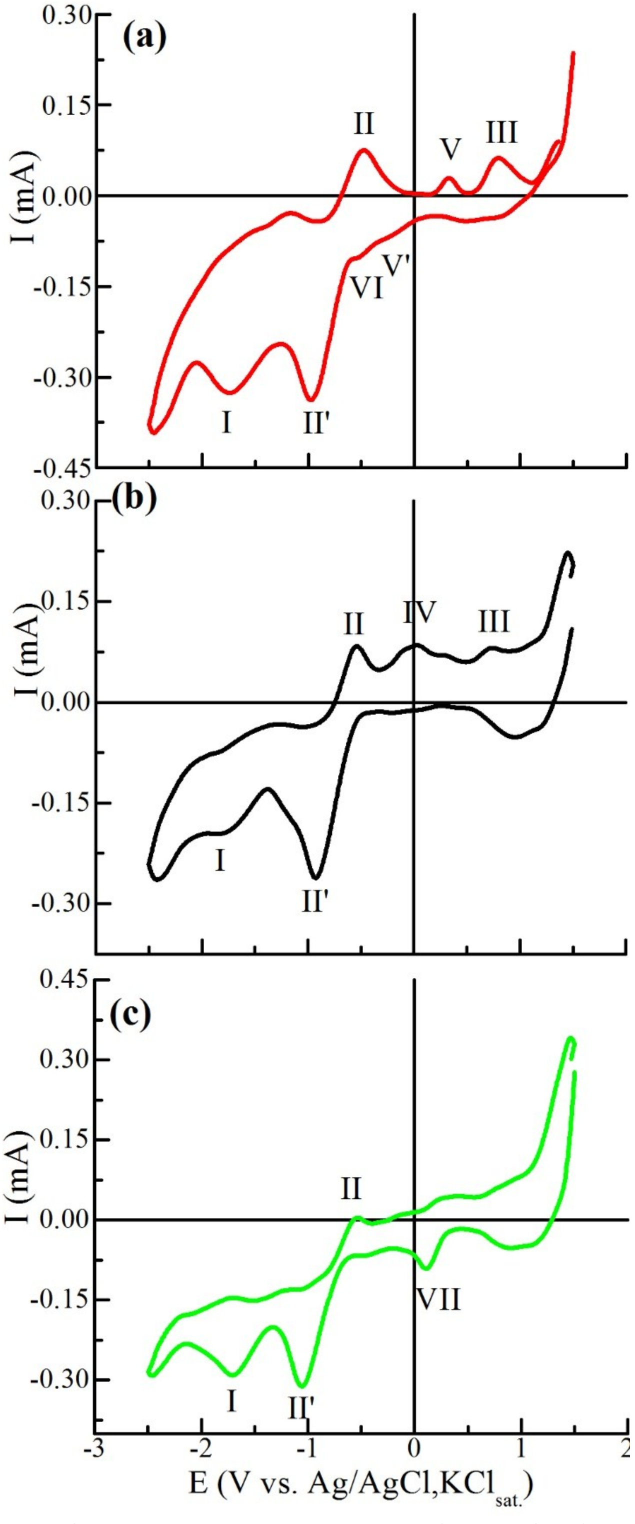


Figure S10. Cyclic voltammograms at GC electrode in acetonitrile solution containing 10 mM TBAP and ligand (panel b) Fe based complex (panel c) and Co-based complex (panel a).

References

1. J. Inczedy, Analitical applications of complex equilibria / J. Inczedy Budapest, 1976
2. M. M. Peixoto, G. F. Bauerfeldt, M. H. Herbst, M. S. Pereira and C. O. da Silva, Journal of Physical Chemistry A, 2015, 119, 5241-5249.
3. T. Baba, T. Matsui, K. Kamiya, M. Nakano and Y. Shigeta, *International Journal of Quantum Chemistry*, 2014, **114**, 1128-1134.
4. T. B. Lee and M. L. McKee, *Physical Chemistry Chemical Physics*, 2011, **13**, 10258-10269.

A. V. Marenich, W. D. Ding, C. J. Cramer and D. G. Truhlar, *Journal of Physical Chemistry Letters*, 2012, **3**, 1437-1442.

A. M. N. Silva, X. L. Kong and R. C. Hider, *Biometals*, 2009, **22**, 771-778.

5. C.P. Kelly, C.J. Cramer, D.G. Truhlar *J. Phys. Chem. B*, 2007, 111, 408-422.
6. M.D. Liptak, G.C. Shields *J. Am. Chem. Soc.*, 2001, 123, 7314–7319.