

Supplementary

Sulfonato complex formation rather than sulfonate binding in the extraction of base metals with 2,2'-biimidazole: extraction and complexation studies

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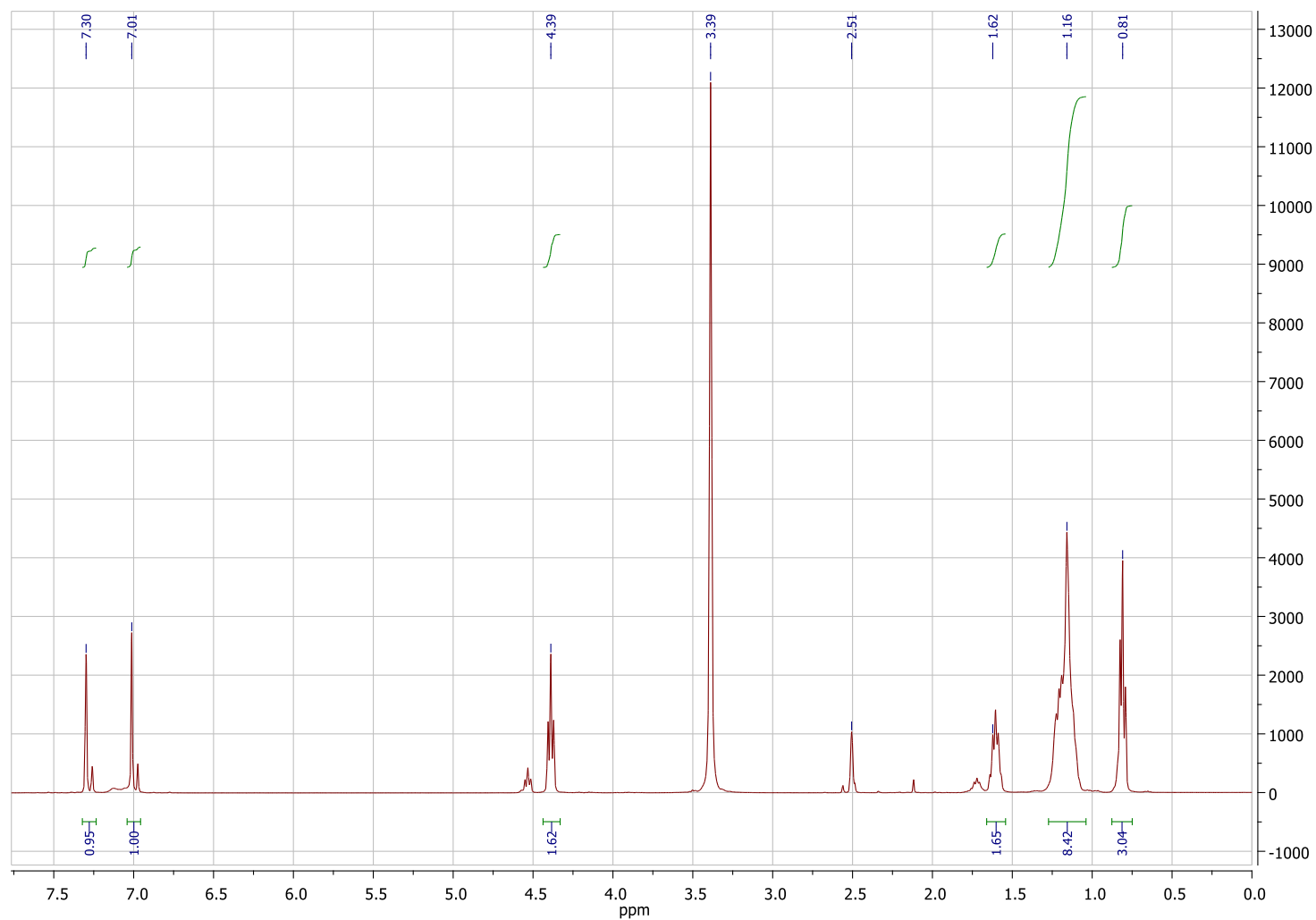


Figure S1: The ^1H NMR spectrum of 1-heptyl-2,2'-biimidazole (HBIIMH).

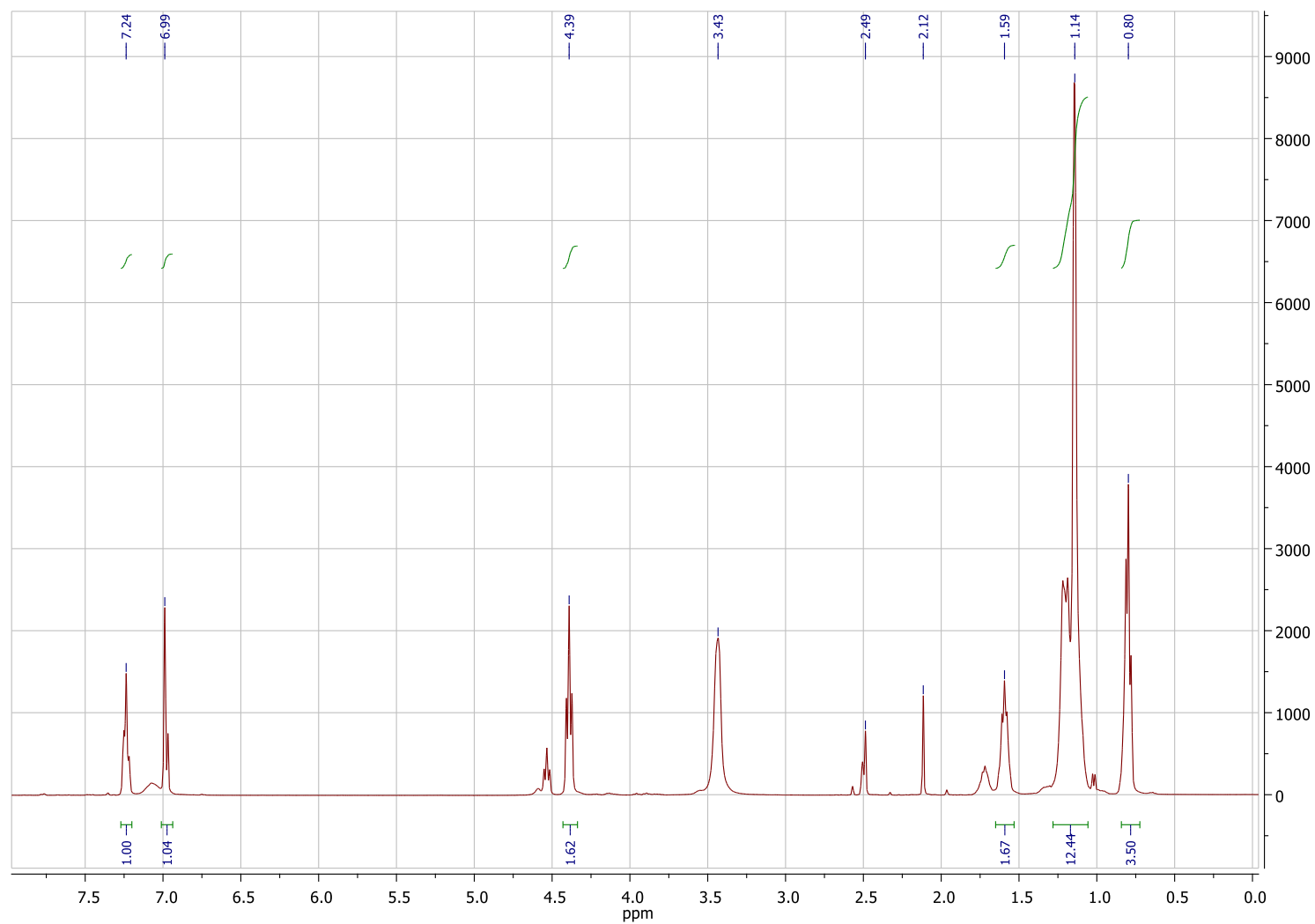


Figure S2: The ^1H NMR spectrum of 1-octyl-2,2'-biimidazole (OBIIMH).

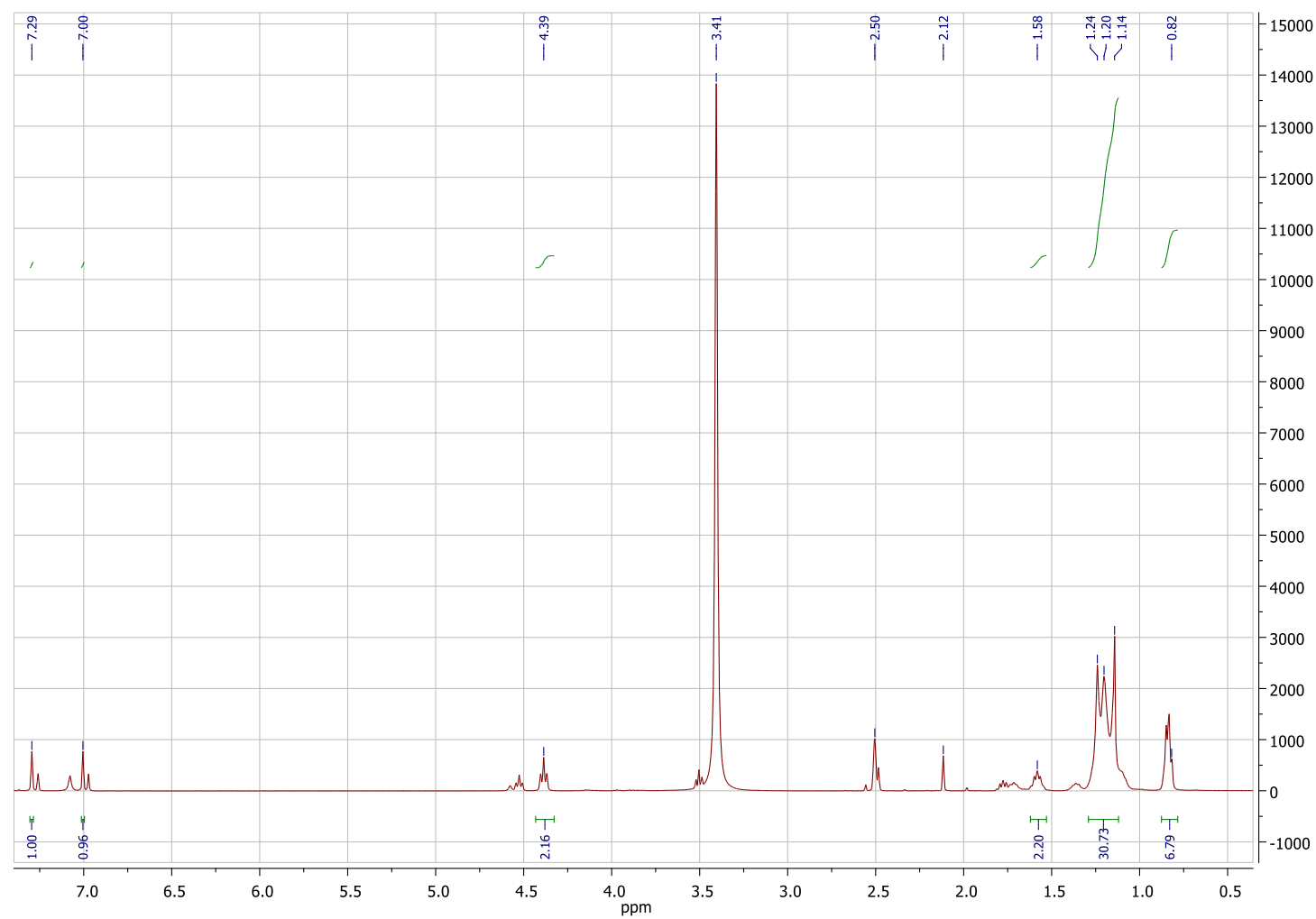


Figure S3: The ^1H NMR spectrum of 1-decyl-2,2'-biimidazole (DBIIMH).

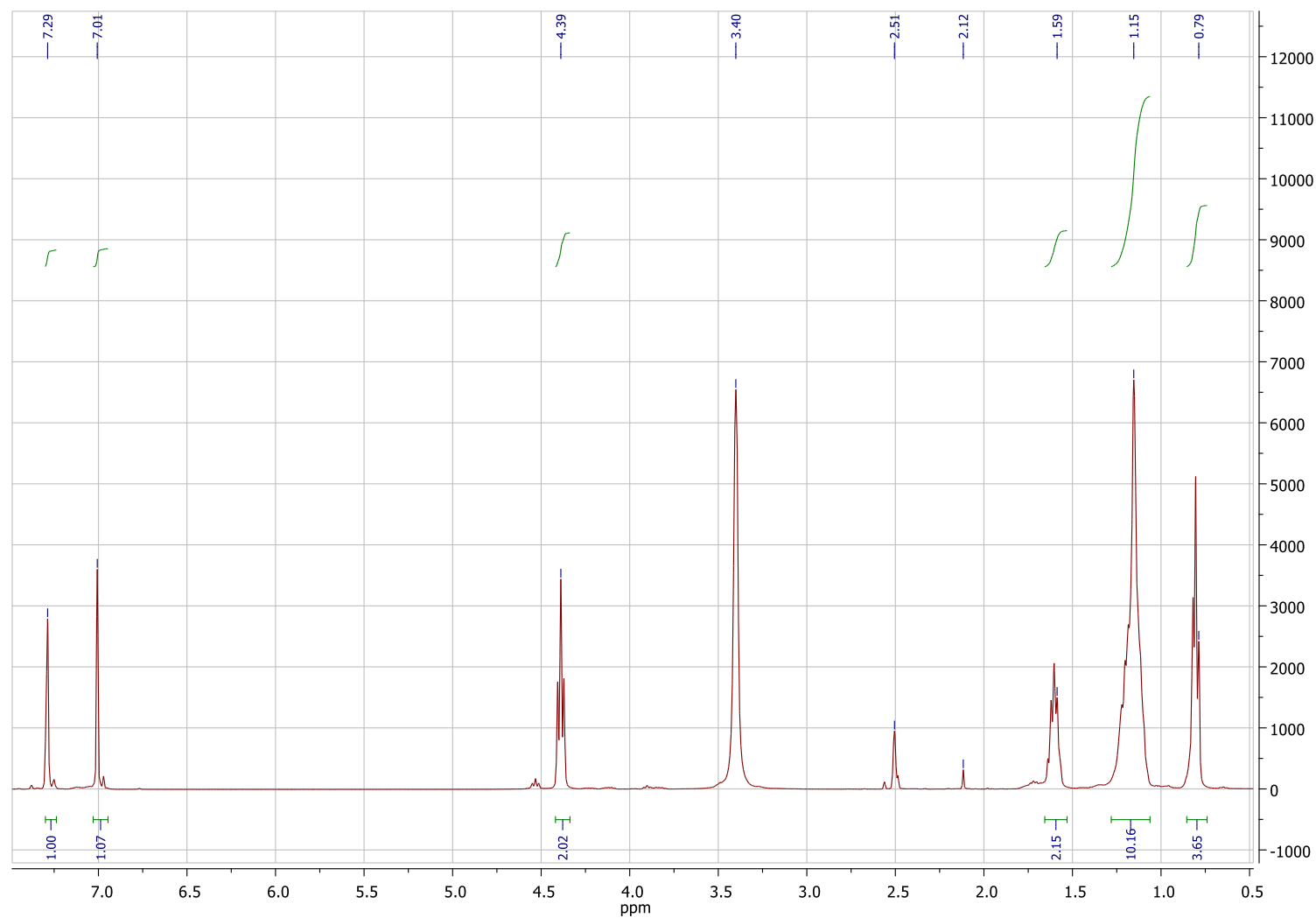


Figure S4: The ^1H NMR spectrum of 1,1'-bis-heptyl-2,2'-biimidazole (H₂BIIM).

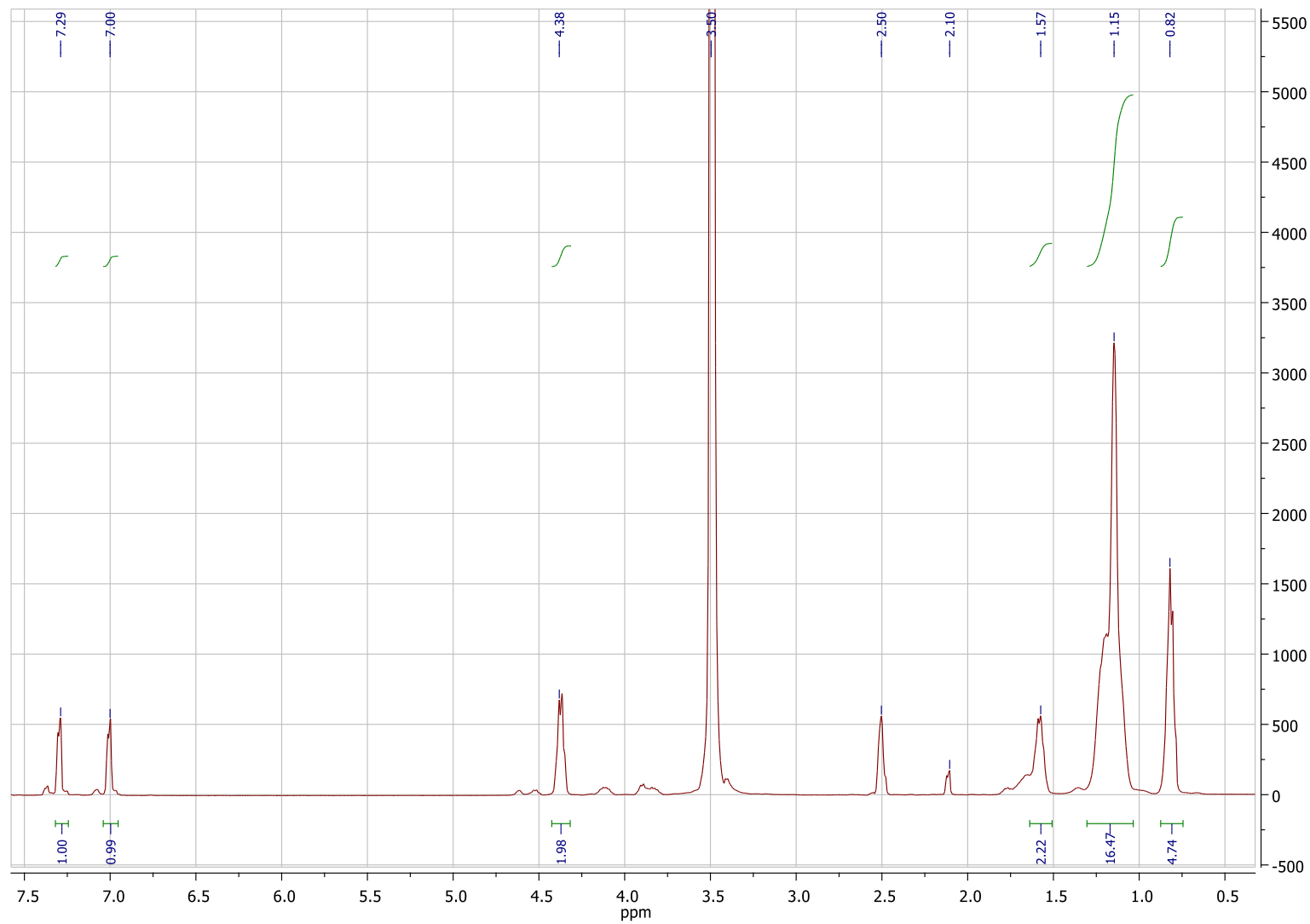


Figure S5: The ^1H NMR spectrum of 1,1'-bis-octyl-2,2'-biimidazole (O₂BIIM).

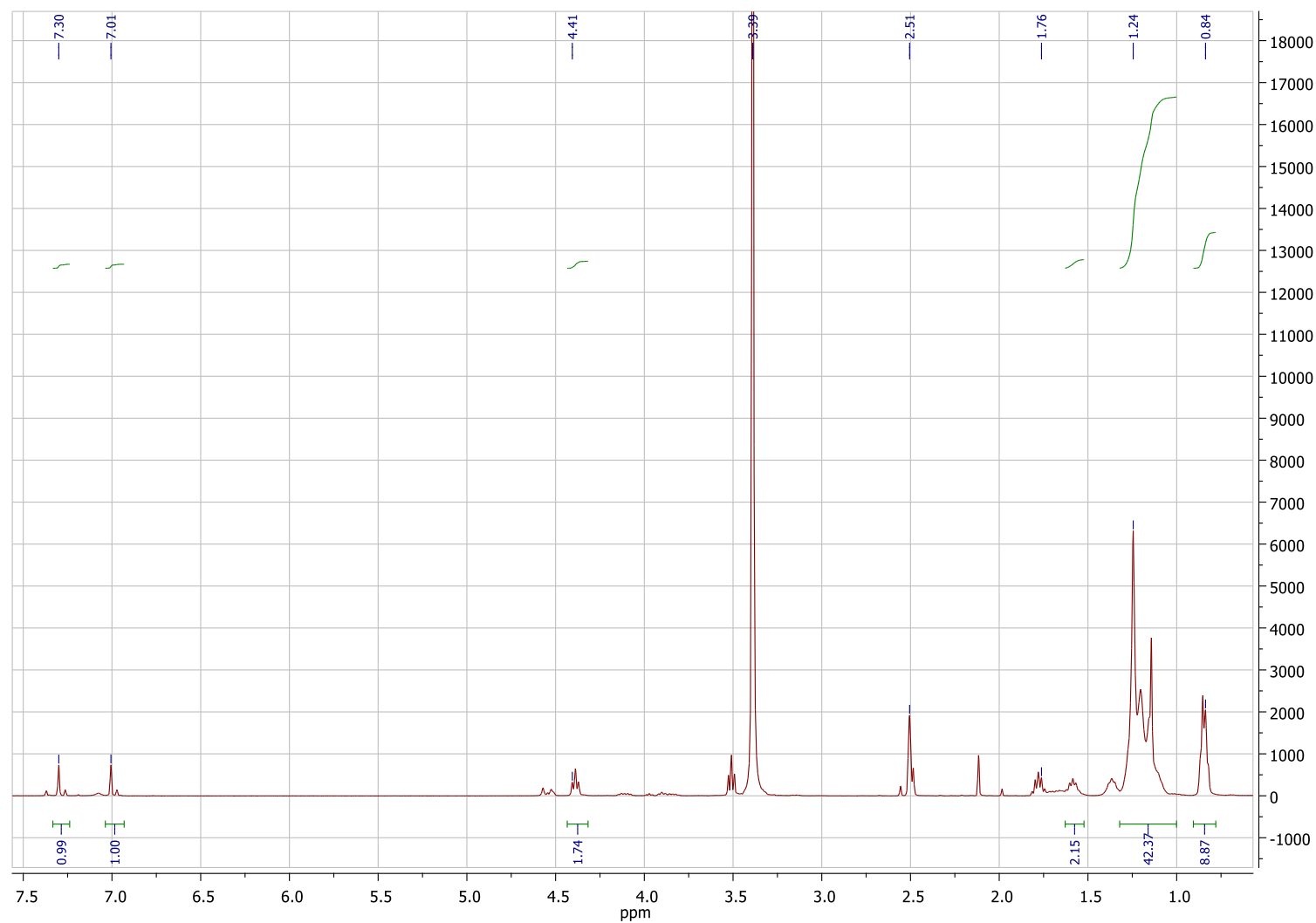


Figure S6: The ^1H NMR spectrum of 1,1'-bis-decyl-2,2'-biimidazole (D₂BIIM).

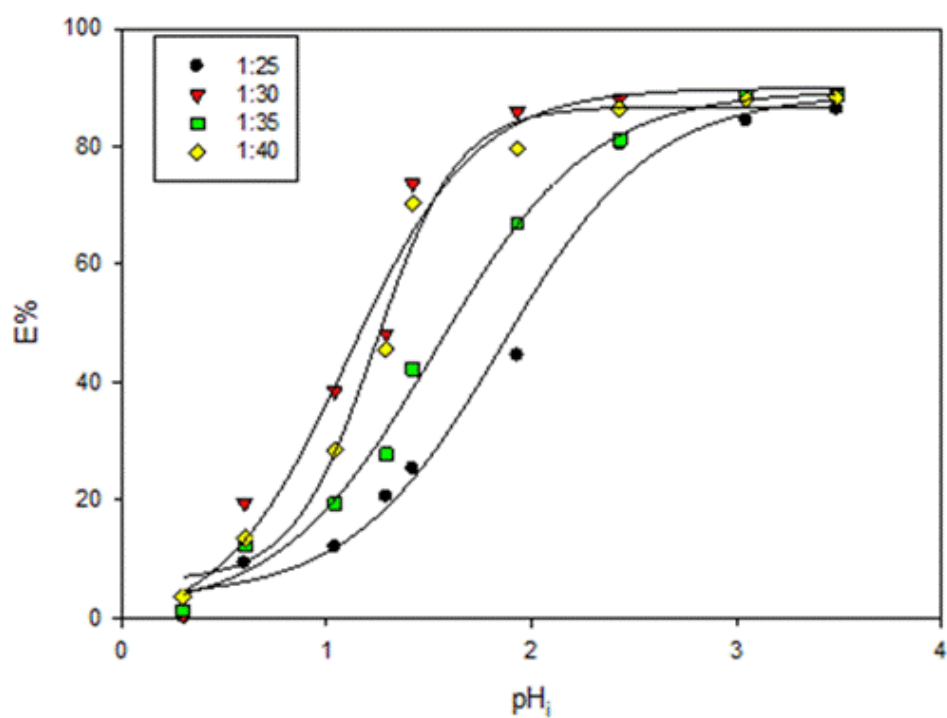


Figure S7: A plot of %E vs initial pH for extraction of 0.001 M nickel from dilute sulfate medium with M:L ratios 1:25, 1:30, 1:35 and 1:40 (Ni:OBIIMH) and 0.5 M DNNDISA in 80% 2-octanol/20% Shellsol 2325.

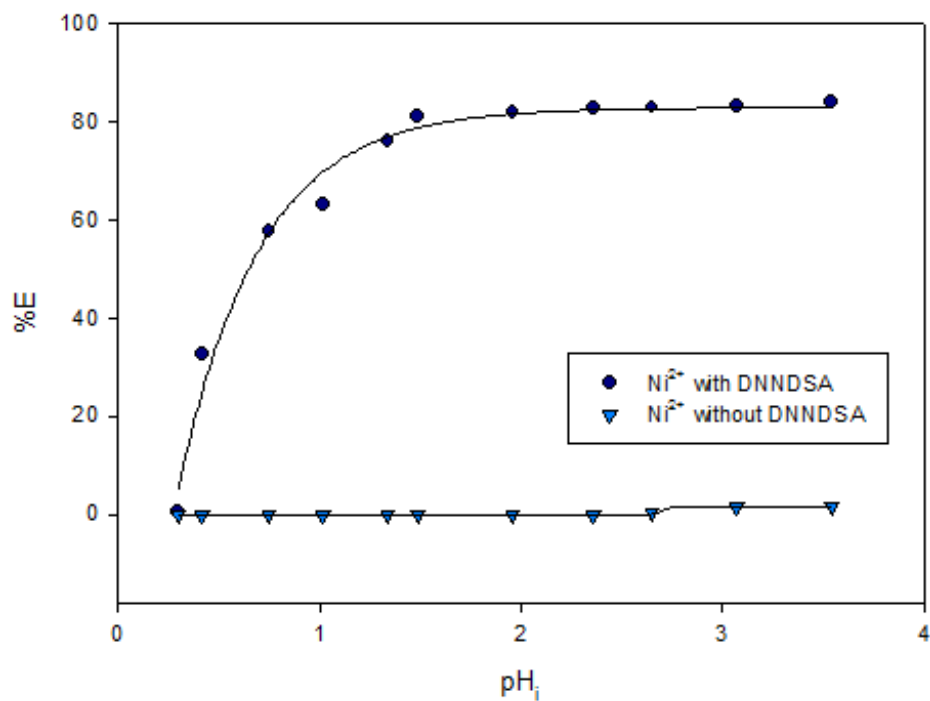


Figure S8: A plot of %E vs initial pH for extraction of 0.001 M nickel from dilute sulfate medium with OBIIMH at M:L molar ratio of 1:30 in the absence of DNNDISA, and with 0.5 M DNNDISA in 80% 2-octanol/20% Shellsol 2325.

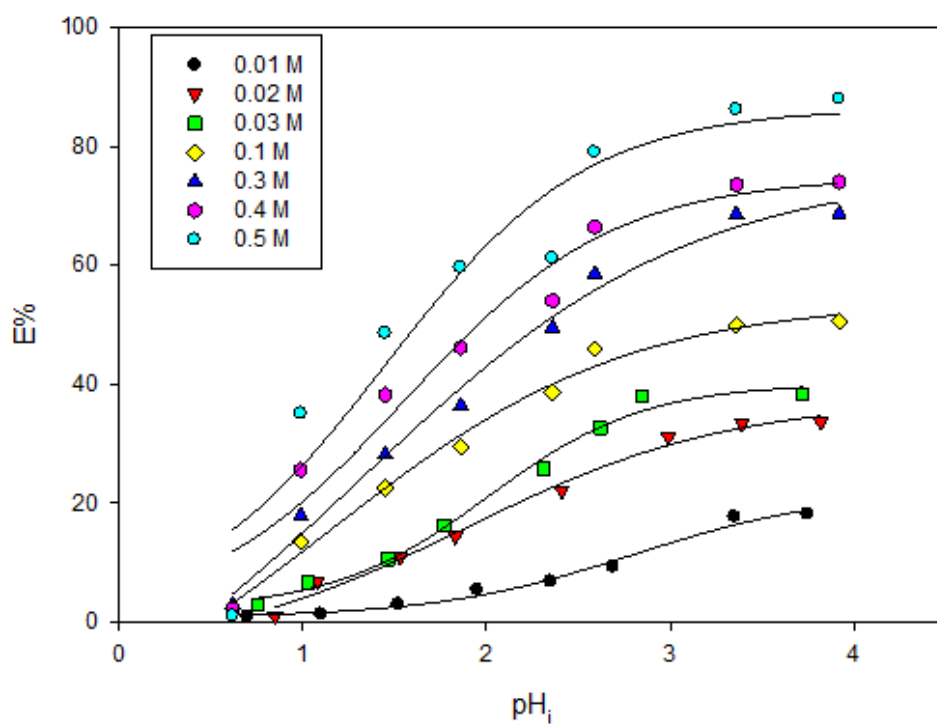


Figure S9: A plot of %E vs initial pH for extraction of 0.001 M nickel from dilute sulfate medium with varying concentration of DNNSA as a synergist in 80% 2-octanol/20% Shellsol 2325.

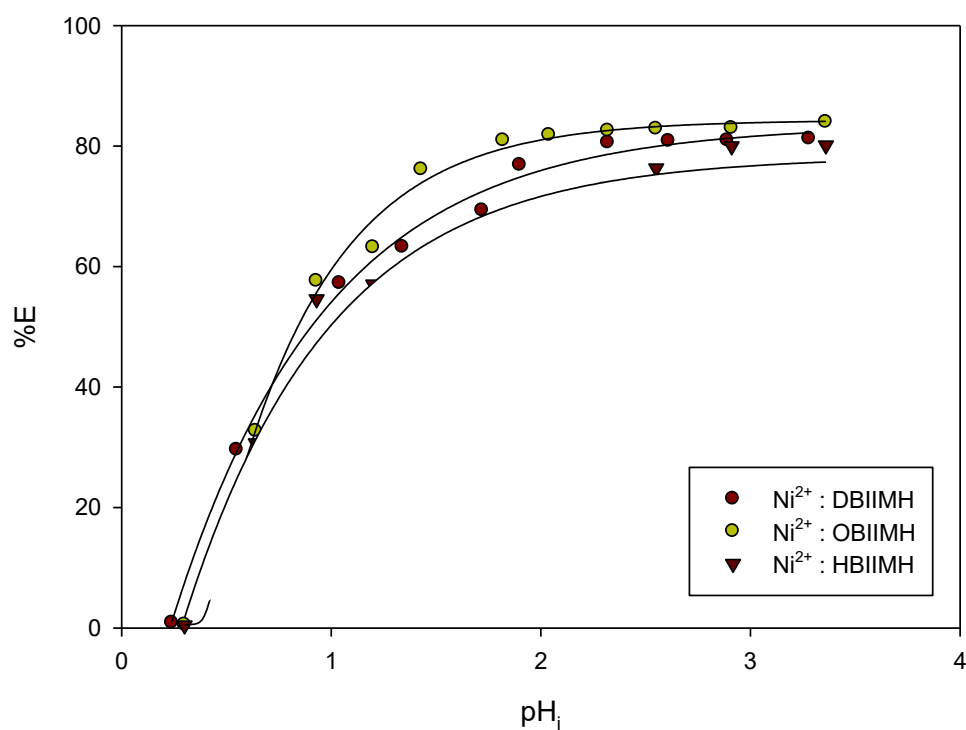


Figure S10: A plot of %E vs initial pH for extraction of 0.001 M nickel from dilute sulfate medium with DBIIMH, OBIIMH and HBIIMH (at Ni:L ratios of 1:30), and 0.5 M DNNSA in 80% 2-octanol/20% Shellsol 2325.

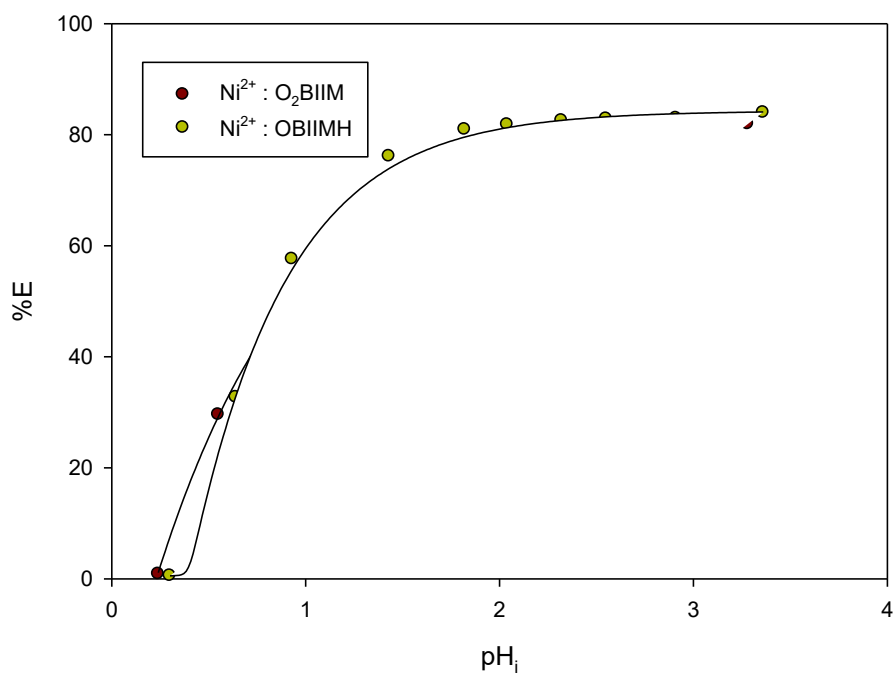


Figure S11: A plot of %E vs initial pH for extraction of 0.001 M nickel from dilute sulfate medium with M:L ratio 1:30 (Ni:OBIIMH and Ni:O₂BIIM) and 0.5 M DNDSA in 80% 2-octanol/20% Shellsol 2325.

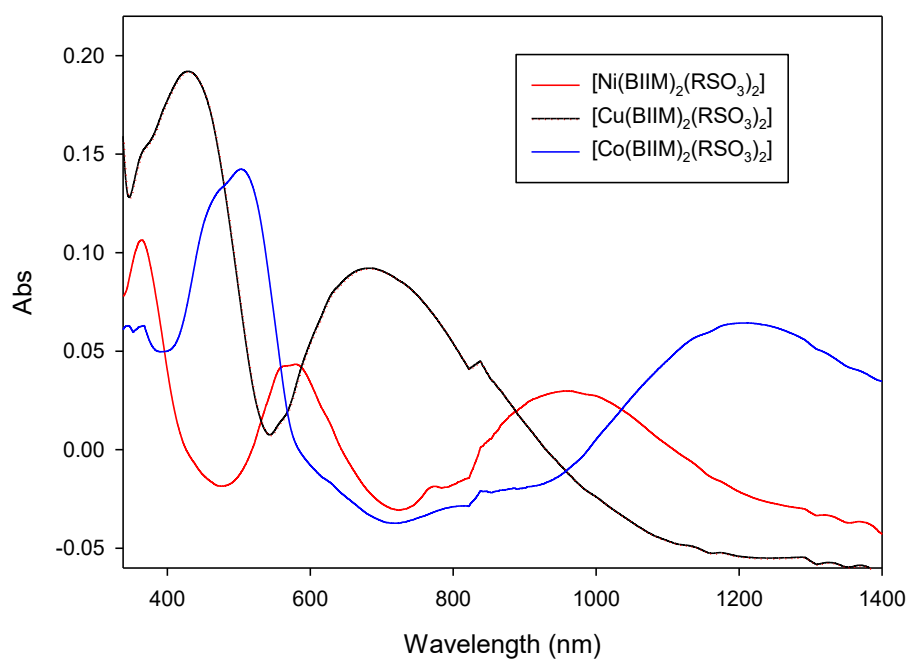


Figure S12: The solid reflectance spectra for nickel(II), cobalt(II) and copper(II) 2,2'-biimidazole complexes in sulfonate medium.

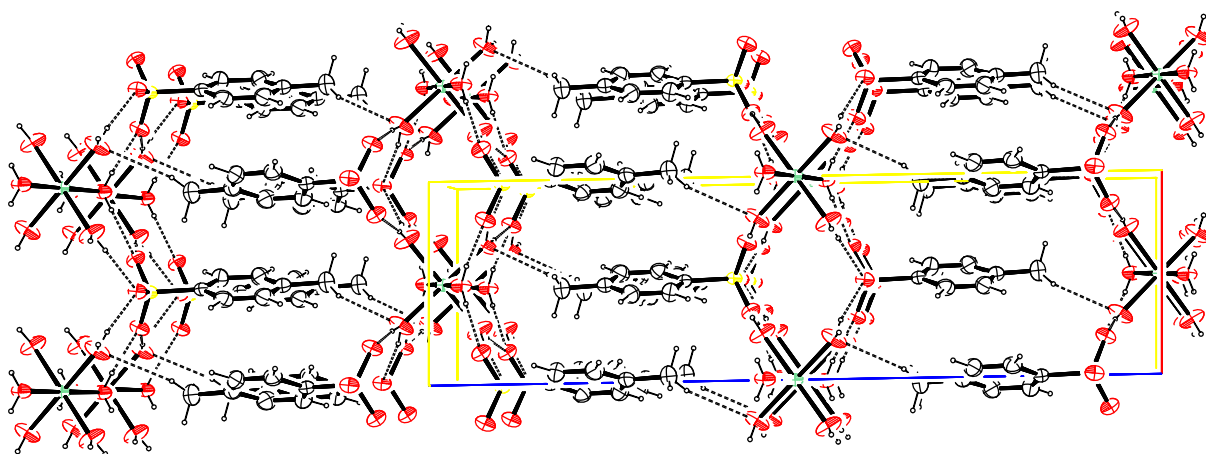


Figure S13: ORTEP packing diagram drawn normal to (0 1 0) showing the alternating planes of complex and anion which lie parallel to the *ab* plane (0 0 1).

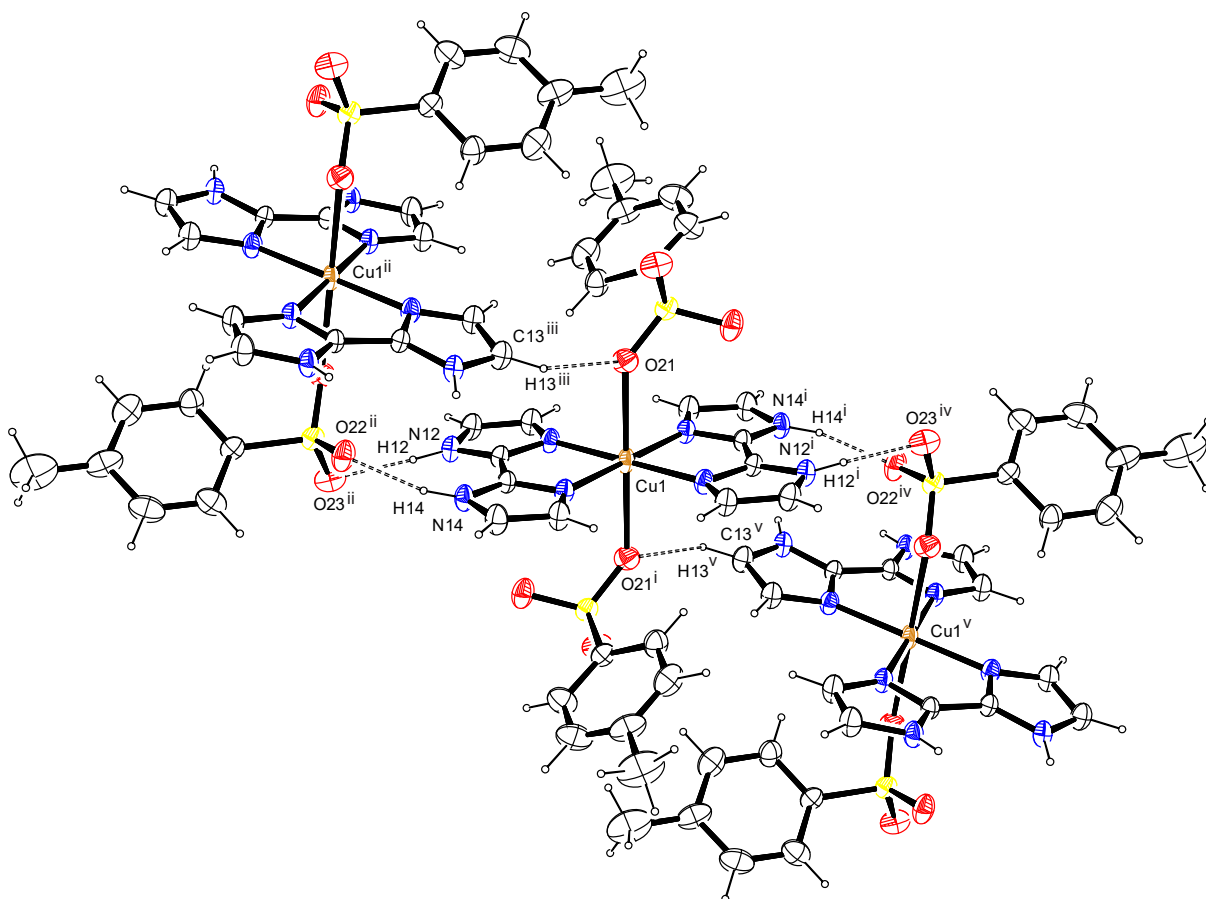


Figure S14: Selected hydrogen interactions with ellipsoids drawn at 50 % probability. Symmetry elements: i) 1-*x*, 1-*y*, 1-*z*; ii) 1-*x*, ½+*y*, ½-*z*; iii) *x*, ½-*y*, -½+*z*; iv) *x*, ½-*y*, ½+*z*; v) 1-*x*, -½+*y*, ½-*z*.

Table S1: Data for %E vs initial and the equilibrium pH of 0.001 M nickel extracted from dilute sulfate medium with M:L ratios 1:25, 1:30, 1:35 and 1:40 (Ni:OBIMH) and 0.5M DNDSA in 80% 2-octanol/ 20% Shellsol 2325.

Ni ²⁺ OBIMH 1:25									
pH_i	0.30	0.60	1.04	1.29	1.42	1.93	2.43	3.05	3.49
pH_e	0.32	0.63	1.00	1.28	1.44	1.96	2.46	3.10	3.44
%E	0.23	9.36	12.05	20.60	25.31	44.56	80.32	84.36	86.27
Ni ²⁺ OBIMH 1:30									
pH_i	0.30	0.60	1.04	1.29	1.42	1.93	2.43	3.05	3.49
pH_e	0.29	0.59	1.03	1.31	1.45	1.97	2.46	3.22	3.56
%E	0.50	19.45	38.45	48.24	73.68	85.94	87.96	88.68	88.99
Ni ²⁺ OBIMH 1:35									
pH_i	0.30	0.60	1.04	1.29	1.42	1.93	2.43	3.05	3.49
pH_e	0.28	0.63	1.09	1.33	1.45	1.96	2.48	3.11	3.62
%E	1.27	12.26	19.46	27.75	42.22	66.96	81.18	88.55	88.60
Ni ²⁺ OBIMH 1:40									
pH_i	0.30	0.60	1.04	1.29	1.42	1.93	2.43	3.05	3.49
pH_e	3.09	0.69	1.10	1.26	1.48	1.90	2.42	3.00	3.58
%E	3.65	13.57	28.53	45.62	70.39	79.65	86.38	88.04	88.31

Table S2: Data for %E vs initial and the equilibrium pH for the extraction of 0.001M nickel from dilute sulfate medium with OBIMH at a M:L molar ratio of 1:30 in the absence of DNDSA, and with 0.5 M DNDSA in 80% 2-octanol/20% Shellsol 2325.

% E Ni ²⁺ with DNDSA											
pH _i	0.30	0.42	0.75	1.02	1.34	1.49	1.96	2.36	2.65	3.07	3.54
pH _e	0.32	0.44	0.72	1.01	1.30	1.43	1.91	2.33	2.59	3.00	3.48
%E	0.53	32.71	57.39	63.18	76.12	80.94	81.82	82.55	82.85	82.98	83.98
% E Ni ²⁺ without DNDSA											
pH _i	0.30	0.42	0.75	1.02	1.34	1.49	1.96	2.36	2.65	3.07	3.54
pH _e	0.31	0.43	0.70	1.00	1.28	1.45	1.93	2.33	2.60	3.02	3.45
%E	0.00	0.01	0.01	0.03	0.05	0.06	0.08	0.08	0.09	1.66	1.59

Table S3: Data for %E vs initial and the equilibrium pH of nickel from dilute sulfate medium with DNNDSA varying concentrations (0.01 M, 0.02 M, 0.03 M, 0.08 M, 0.1 M, 0.3 M, 0.4 M and 0.5 M) of Ni²⁺:OBIMH (1:30) in 80% 2-octanol/Shellsol 2325.

0.01 M DNNDSA								
pH _i	0.70	1.10	1.52	1.95	2.35	2.69	3.35	3.75
pH _e	0.65	1.15	1.56	1.82	2.44	2.73	3.29	3.64
%E	0.95	1.36	3.03	5.42	6.85	9.37	17.70	18.17
0.02 M DNNDSA								
pH _i	0.85	1.08	1.53	1.83	2.41	2.99	3.39	3.82
pH _e	0.92	1.02	1.62	1.86	2.38	2.85	3.32	3.89
%E	1.03	6.92	10.96	14.44	22.16	31.15	33.44	33.63
0.03 M DNNDSA								
pH _i	0.75	1.03	1.46	1.77	2.31	2.62	2.85	3.72
pH _e	0.70	1.13	1.44	1.82	2.36	2.69	2.89	3.76
%E	2.99	6.69	10.65	16.31	25.90	32.69	37.96	38.35
0.08 M DNNDSA								
pH _i	0.75	0.98	1.12	1.36	1.53	1.92	2.34	4.04
pH _e	0.79	0.92	1.26	1.49	1.68	1.83	2.41	4.00
%E	1.65	6.65	10.96	18.33	31.63	46.28	46.73	47.18
0.1 M DNNDSA								
pH _i	0.62	0.99	1.45	1.86	2.36	2.59	3.36	3.92
pH _e	0.69	0.92	1.56	1.92	2.41	2.60	3.43	3.89
%E	2.33	13.56	22.63	29.53	38.63	45.96	49.96	50.63
0.3 M DNNDSA								
pH _i	0.62	0.99	1.45	1.86	2.36	2.59	3.36	3.92
pH _e	0.72	1.06	1.58	1.88	2.39	2.65	3.37	3.85
%E	3.02	18.00	28.24	36.45	49.55	58.62	68.56	68.71

Table S3: Continued.

0.4 M DNND SA								
pH_i	0.62	0.99	1.45	1.86	2.36	2.59	3.36	3.92
pH_e	0.66	1.05	1.40	1.92	2.33	2.65	3.40	3.90
%E	2.31	25.63	38.23	46.23	54.06	66.45	73.56	74.06
0.5 M DNND SA								
pH_i	0.62	0.99	1.45	1.86	2.36	2.59	3.36	3.92
pH_e	0.68	1.13	1.58	1.96	2.49	2.55	3.42	3.95
%E	1.07	35.06	48.56	59.57	61.20	78.97	86.02	87.96

Table S4: Data for the extraction of nickel (0.001 M) from dilute sulfate medium with DBIIMH, OBIIMH and HBIIMH at M:L ratios of 1:30, respectively, and 0.5 M DNND SA in 80% 2-octanol/20% Shellsol 2325.

Ni ²⁺ : DBIIMH											
pH _i	0.24	0.55	1.04	1.34	1.72	1.90	2.32	2.61	2.89	3.28	
pH _e	0.32	0.62	1.12	1.39	1.78	1.96	2.40	2.68	2.73	3.22	
%E	0.86	29.56	57.23	63.24	69.30	76.86	80.56	80.84	80.94	81.23	
Ni ²⁺ : OBIIMH											
pH _i	0.30	0.64	0.93	1.20	1.43	1.82	2.04	2.32	2.55	2.91	3.36
pH _e	0.39	0.58	0.95	1.18	1.49	1.86	2.04	2.36	2.50	2.96	3.42
%E	0.56	32.71	57.59	63.18	76.12	80.94	81.82	82.55	82.85	82.98	83.98
Ni ²⁺ : HBIIMH											
pH _i	0.30	0.64	0.93	1.20	1.43	1.82	2.04	2.32	2.55	2.91	3.36
pH _e	0.35	0.56	0.96	1.25	1.49	1.88	2.20	2.41	2.61	2.86	3.38
%E	0.43	30.68	54.56	57.02	61.41	63.46	68.45	73.23	76.31	79.98	80.10

Table S5: Data for %E vs initial and the equilibrium pH of 0.001 M nickel extracted from dilute sulfate medium with M:L ratio of 1:30 (Ni:OBIIIMH and O₂BIIM) and 0.5 M DNNDSA in 80% 2-octanol/20% Shellsol 2325.

Ni: OBIIIMH											
pH_i	0.30	0.64	0.93	1.20	1.43	1.82	2.04	2.32	2.55	2.91	3.36
pH_e	0.31	0.65	0.96	1.21	1.48	1.90	2.09	2.41	2.62	2.98	3.35
%E	0.56	32.71	57.59	63.18	76.12	80.94	81.82	82.55	82.85	82.98	83.98
Ni: O ₂ BIIM											
pH_i	0.24	0.55	1.04	1.34	1.72	1.90	2.32	2.61	2.89	3.28	
pH_e	0.26	0.53	1.14	1.39	1.80	1.89	2.39	2.56	2.91	3.24	
%E	0.86	29.56	57.23	63.24	69.30	76.86	80.56	80.82	81.23	81.91	

Table S6: Data for %E vs initial and the equilibrium pH of equimolar concentrations (0.001 M) of Ni²⁺, Co²⁺, Cu²⁺, Fe²⁺, Zn²⁺, Fe³⁺, Mn²⁺, Mg²⁺, Cd²⁺, and Ca²⁺ extracted with OBIIMH at M:L ratio (1:30) and 0.5 M DNNDISA in 80% 2-octanol/20% Shellsol 2325 from sulfate medium.

Ni ²⁺										
pH _i	0.64	0.93	1.20	1.43	1.82	2.04	2.32	2.55	2.91	3.36
pH _e	0.69	0.99	1.26	1.56	1.94	2.15	2.36	2.53	2.99	3.33
%E	6.71	57.59	63.18	76.12	80.94	81.82	85.55	87.85	87.98	88.98
Co ²⁺										
pH _i	0.31	0.52	0.94	1.28	1.56	1.88	2.18	2.47	2.95	3.47
pH _e	0.39	0.69	1.06	1.36	1.65	1.95	2.27	2.56	3.00	3.54
%E	3.52	17.63	36.44	44.56	55.63	56.79	59.13	59.57	60.48	60.84
Cu ²⁺										
pH _i	0.35	0.59	1.06	1.29	1.69	2.08	2.38	2.91	3.47	
pH _e	0.42	0.72	1.19	1.35	1.70	2.19	2.48	2.98	3.52	
%E	4.96	27.21	53.44	60.39	68.28	75.86	78.06	78.88	79.47	
Zn ²⁺										
pH _i	0.75	1.25	1.51	1.80	2.00	2.27	2.56	2.73	3.10	3.41
pH _e	0.88	1.32	1.60	1.86	2.10	2.35	2.61	2.81	3.18	3.50
%E	3.16	38.21	40.51	62.45	72.76	73.02	73.15	73.33	73.40	73.52
Mn ²⁺										
pH _i	0.49	1.09	1.20	1.43	1.60	1.81	2.08	2.35	2.68	2.92
pH _e	0.56	1.15	1.26	1.43	1.65	1.86	2.16	2.42	2.75	2.98
%E	0.20	34.52	38.63	43.66	50.96	58.62	60.86	61.02	61.37	62.60
Cd ²⁺										
pH _i	0.49	1.09	1.20	1.43	1.60	1.81	2.08	2.35	2.68	2.92
pH _e	0.60	1.19	1.28	1.52	1.65	1.90	2.23	2.49	2.76	3.10
%E	0.00	49.20	53.22	70.61	78.26	85.57	93.06	93.57	93.85	96.75
Fe ³⁺										
pH _i	0.34	1.00	1.25	1.56	1.86	2.18	2.36	2.57	2.78	3.12
pH _e	0.42	1.11	1.36	1.66	1.95	2.26	2.42	2.66	2.89	3.26
%E	0.00	49.36	74.22	76.87	82.05	82.57	84.01	85.40	85.70	85.93

Table S6: Continued.

Fe²⁺										
pH_i	0.49	1.09	1.20	1.43	1.60	1.81	2.08	2.35	2.68	2.92
pH_e	0.56	1.12	1.23	1.50	1.69	1.95	2.28	2.46	2.79	3.01
%E	0.29	46.25	52.53	69.96	75.26	80.53	82.36	82.96	83.59	83.75
Mg²⁺										
pH_i	0.64	1.24	1.53	1.72	1.98	2.28	2.40	2.57	2.84	3.12
pH_e	0.69	1.36	1.68	1.82	2.05	2.36	2.45	2.69	2.96	3.24
%E	10.43	67.12	72.89	74.16	74.44	74.63	74.84	75.88	75.92	77.26
Ca²⁺										
pH_i	0.49	1.09	1.20	1.43	1.60	1.81	2.08	2.35	2.68	2.92
pH_e	0.66	1.12	1.35	1.50	1.66	1.86	2.21	2.56	2.76	3.05

Table S7: Data for %E vs initial and the equilibrium pH of equimolar concentrations (0.001 M) of Ni^{2+} , Co^{2+} , Cu^{2+} , Fe^{2+} , Zn^{2+} , Fe^{3+} , Mn^{2+} , Mg^{2+} , Cd^{2+} , and Ca^{2+} extracted with OPIM at M:L ratio (1:25) and 0.015 M DNNSA in 80% 2-octanol/20% Shellsol 2325 from sulfate medium.

Ni^{2+}								
pH_i	0.40	0.60	1.04	1.29	1.63	1.90	2.21	2.57
pH_e	0.59	0.78	1.01	1.20	1.27	1.46	1.56	1.64
% E	0.50	3.46	11.45	28.24	80.94	95.33	97.48	97.69
Co^{2+}								
pH_i	1.65	1.87	2.17	2.43	2.77	3.08	3.49	
pH_e	1.23	1.33	1.87	2.17	2.43	2.77	3.08	
% E	0.02	0.02	5.71	19.38	42.16	51.07	58.92	
Cu^{2+}								
pH_i	0.65	1.04	1.48	2.00	2.63	2.95	1.13	
pH_e	0.62	0.80	1.02	1.50	2.09	2.69	2.95	
% E	0.91	3.99	11.57	35.61	66.18	77.18	0.00	
Fe^{2+}								
pH_i	1.13	1.66	2.06	2.46	2.80	2.94	3.30	
pH_e	1.15	1.69	2.05	2.16	2.85	2.87	2.90	
% E	0.00	0.06	1.85	12.87	41.87	52.24	61.54	
Zn^{2+}								
pH_i	0.51	1.02	1.44	1.83	2.11	2.54	2.91	
pH_e	0.76	1.05	1.47	1.88	2.25	2.81	3.22	
% E	0.00	0.00	0.00	0.00	0.00	3.08	20.28	
Mn^{2+}								
pH_i	1.01	1.37	1.75	2.16	2.53	2.84	3.22	
pH_e	1.02	1.40	1.79	2.30	2.74	3.16	3.57	
% E	0.74	0.80	0.84	1.05	1.79	3.42	6.09	
Mg^{2+}								
pH_i	0.52	1.04	1.57	2.12	2.44	2.78	3.15	
pH_e	0.54	1.06	1.60	2.34	2.66	3.10	3.50	
% E	0.00	0.00	0.00	0.00	0.04	0.83	1.31	
Cd^{2+}								
pH_i	0.46	0.80	1.21	1.59	1.98	2.47	2.95	
pH_e	0.49	0.86	1.28	1.60	2.05	2.65	3.13	
% E	0.00	0.00	0.00	0.00	3.84	15.69	20.99	
Fe^{3+}								
pH_i	0.98	1.51	1.98	2.36				
pH_e	0.85	1.15	1.72	2.19				
% E	0.00	0.00	0.09	0.94				
Ca^{2+}								
pH_i	0.41	0.74	1.32	2.05	2.54	3.09	3.57	
pH_e	0.40	0.72	1.22	1.95	2.34	3.89	3.38	
% E	0.00	0.00	0.0	0.94	0.64	1.34	3.67	

Table S8: A plot of %E vs initial and the equilibrium pH for 0.001 M Ni²⁺, Co²⁺, Cu²⁺, Fe²⁺, Zn²⁺, Mn²⁺, Mg²⁺ and Fe³⁺ from dilute sulfate medium with OBIMA (M:L ratios of 1:40), and 0.015 M DNNSA in 80% 2-octanol/20% Shellsol 2325.

Ni²⁺								
pH_i	0.50	0.96	1.24	1.57	1.63	1.87	2.20	2.5
pH_e	0.59	0.98	1.17	1.39	1.41	1.64	2.19	2.15
% E	0.51	4.46	27.18	73.59	88.63	96.00	96.46	96.63
Co²⁺								
pH_i	0.54	0.92	1.27	1.53	2.08	2.56	3.07	3.49
pH_e	0.51	0.97	1.13	1.47	1.73	2.32	2.71	2.92
% E	0.00	0.09	0.07	0.54	9.00	35.38	58.81	61.88
Cu²⁺								
pH_i	0.54	1.24	1.55	2.07	2.27	2.53	3.05	3.42
pH_e	0.51	1.19	1.36	1.89	2.04	2.23	2.86	2.91
% E	0.74	1.27	13.67	27.51	49.02	61.10	67.06	68.30
Zn²⁺								
pH_i	0.52	0.87	1.85	2.03	2.42	2.80	3.07	3.60
pH_e	0.55	0.89	1.74	1.97	2.17	2.23	2.73	2.88
% E	0.17	0.29	0.64	2.13	11.61	20.63	34.82	55.15
Mn²⁺								
pH_i	0.52	0.87	1.85	2.03	2.35	2.92	3.29	3.47
pH_e	0.56	0.92	1.76	1.96	2.09	2.65	2.77	2.61
% E	0.10	0.18	0.90	2.00	3.86	16.09	26.51	27.00
Mg²⁺								
pH_i	0.52	0.87	1.85	2.03	2.41	2.98	3.29	3.47
pH_e	0.56	0.91	1.64	1.87	2.25	2.62	2.98	2.76
% E	0.12	0.67	1.58	1.84	1.94	10.61	19.01	22.84
Fe³⁺								
pH_i	0.52	0.87	1.85	2.03	2.35	2.92	3.29	3.47
pH_e	0.56	0.83	1.97	1.96	2.01	2.64	2.81	2.97
% E	0.08	0.09	0.85	0.94	0.98	1.10	14.43	15.54