Cobaloximes with Dimesitylglyoxime: Synthesis, Characterization and Spectral Correlations with the Related Cobaloximes

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Supporting Information

Tables

^{1}H of free Py; α = 8.57, β = 7.05, γ = 7.43

Table ST1. Coordination shifts $\Delta\delta$ ($\Delta\delta^1H = \delta^1H_{complex} - \delta^1H_{free\ pyridine}$) for Py_α of **1-9.**

X	gH	dmgH	chgH	dpgH	mestgH
1	0.04	0.02	-0.01	0.43	0.42
2	0.03	-0.01	-0.01	0.30	0.38
3	0.03	0.00	-0.01	0.33	0.38
4	0.04	0.03	0.05	0.33	0.39
5		-0.03	0.02	0.30	0.41
6	-0.32	-0.32	-0.31	0.02	0.09
7	-0.34	-0.32	-0.32	0.02	0.09
8	-0.28	-0.25	-0.27	0.07	0.11
9	-0.26	-0.29	-0.25	0.07	0.09

Table ST2. Coordination shifts $\Delta\delta^1H$ for Py_β

R/X	gH	dmgH	chgH	dpgH	mestgH
1	0.34	0.26	0.19	-	0.36
2	0.33	0.20	0.22	-	0.35
3	0.33	0.24	0.26	-	0.35
4	0.33	0.26	0.23	-	0.35
5		0.19	0.20	-	0.31
6	0.26	0.21	0.22	0.31	0.29
7	0.27	0.21	0.21	0.36	0.29
8	0.29	0.22	0.19	0.36	0.34
9	0.29	0.18	0.23	0.34	0.31

Table ST3. Coordination shifts $\Delta\delta^1H$ for Py_γ

R/X	gH	dmgH	chgH	dpgH	mestgH
1	0.37	0.22	0.22	0.44	0.45
2	0.36	0.21	0.22	0.32	0.43
3	0.36	0.28	0.32	0.35	0.43
4	0.35	0.29	0.22	0.35	0.43
5		0.16	0.22	-0.18	0.39
6	0.35	0.30	0.31	0.40	0.44
7	0.36	0.27	0.30	0.41	0.44
8	0.38	0.30	0.29	0.43	0.48
9	0.37	0.27	0.32	0.42	0.45

Table ST4. Coordination shifts Δδ ($\Delta\delta^{13}C_{C=N} = \delta^{13}C_{complex} - \delta^{13}C_{free\ dioxime}$) for C=N of **1-9.**

R/X	gH	dmgH	chgH	dpgH	mestgH
1	-7.43	-5.24	-3.06	-4.35	-2.47
2	-7.44	-5.24	-3.06	-4.40	-2.34
3	-7.34	-5.09	-3.03	-4.55	-2.35
4	-7.44	-5.16	-3.06	-4.45	-2.37
6	-4.81	-3.10	-1.92	-1.67	0.77
7	-4.27	-3.42	-2.25	-1.20	1.20
8	-4.89	-3.51	-2.28	-1.53	0.95
9	-5.52	-2.87	-1.69	-1.91	0.72

Table ST5. X-Ray data comparison of $MeCo(dmestgH)_2Py$, MeCo((dpgH)Py[9d], $MeCo(gH)_2Py$[23a], $MeCo(dmgH)_2Py$[23b], MeCo[(DO)(DOH)pn]Py[23b] and MeCbls[2c]

	Co-C	Co-N(ax)	α (^{0})[a]	d (Å)	τ (twist) (^{0})	C-Co-N(ax)
$MeCo(dmestgH)_2Py$	2.002(3)	2.085(3)	7.25(2)	-0.0177(4)	67.09	178.33(11)
$MeCo(dpgH)_2Py$	1.997(4)	2.053(4)	4.7	0.05	76.8	180
$MeCo(dmgH)_2Py$	1.998(5)	2.068(3)	3.2	0.04	88.78	178.0 (2)
$MeCo(gH)_2Py$	2.005(4)	2.064(3)	1.95	0.05	89.62	178.0 (2)
MeCo[(DO)(DOH)pn]Py	2.003(3)	2.106(3)	6.9	0.07	0	
Me-Cbls	1.99(2)	2.19(2)				171(2)

Table ST6. X-Ray data comparison of $ClCo(dmestgH)_2Py$ (6), and $BrCo(dmestgH)_2Py$ (7) with $ClCo((dpgH)_2Py$[24a], $ClCo(dmgH)_2Py$[24b]

	Co-X	Co-N(ax)	α (^{0})[a]	d (Å)	τ (twist) (^{0})	X-Co-N5
$ClCo(dmestgH)_2Py$	2.2243(15)	1.978 (3)	6.57 (1)	-0.009 (6)	69.50	177.99 (12)
$BrCo(dmestgH)_2Py$	2.3396(12)	1.986(4)	6.18 (1)	-0.014 (1)	70.37	177.67 (10)
$ClCo(dpgH)_2Py$	2.235(2)	1.965(3)			85.9	178.2(1)
$ClCo(dmgH)_2Py$	2.229 (1)	1.959 (2)	3.6 (0)	-0.003 (1)	-	179.82

[a] value calculated.

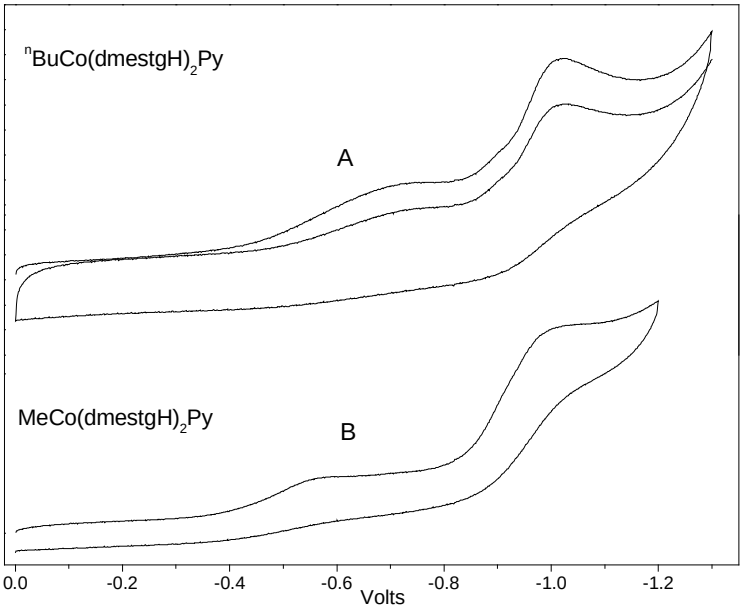

Fig S2. CV showing the reductive half of **1** and **4**.

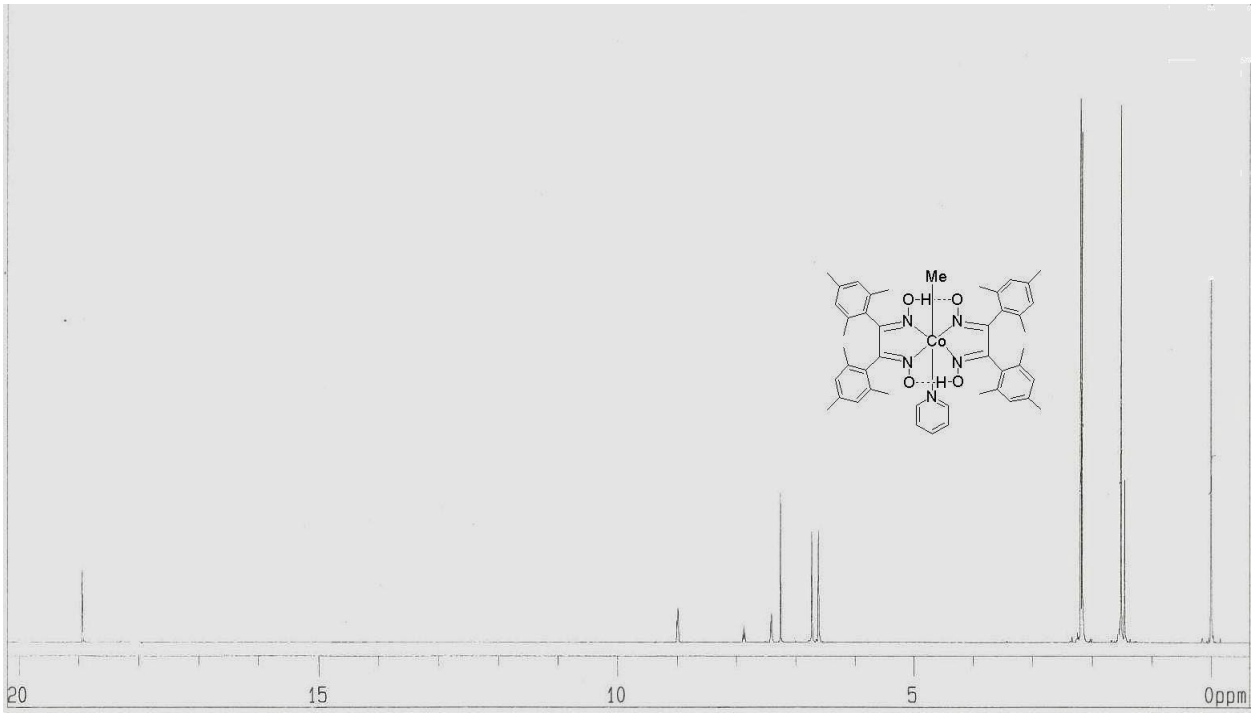

Fig S3. 400 MHz ^{1}H NMR of **1.**

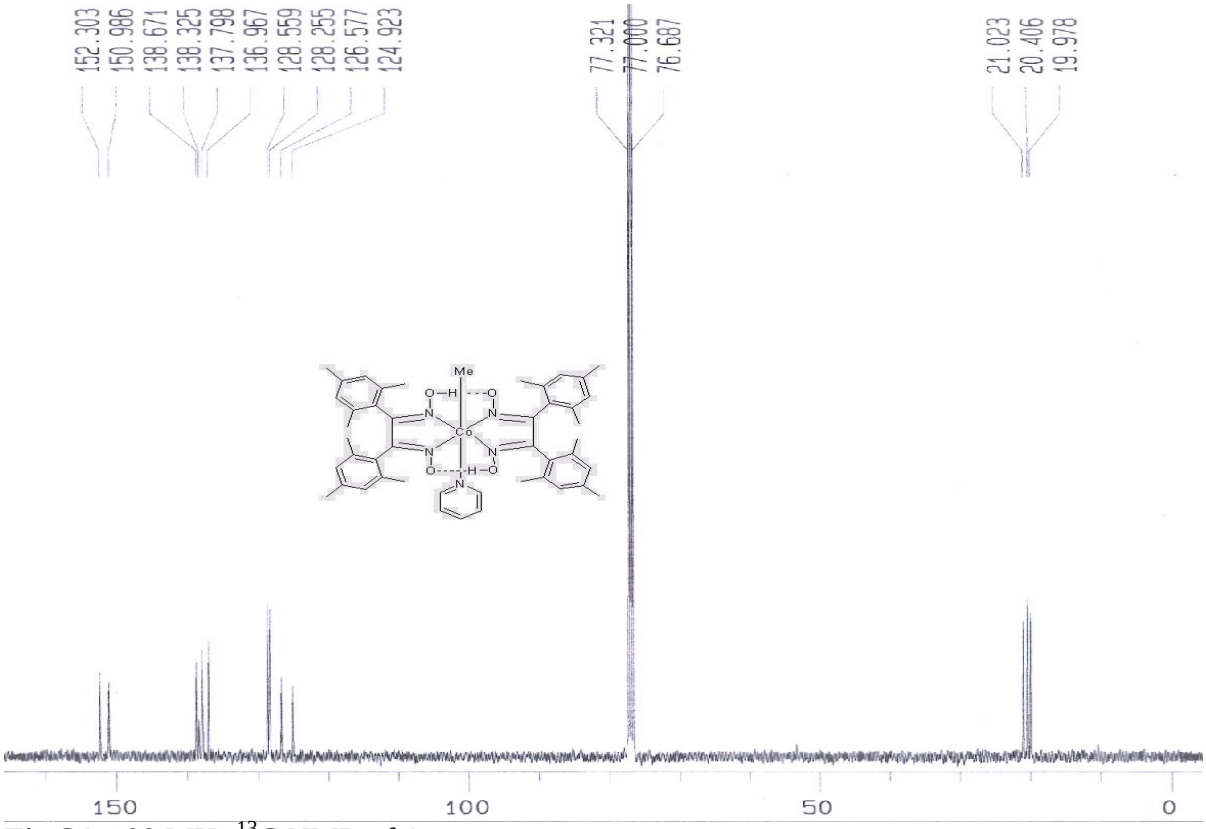

Fig S4. 100 MHz ^{13}C NMR of **1.**

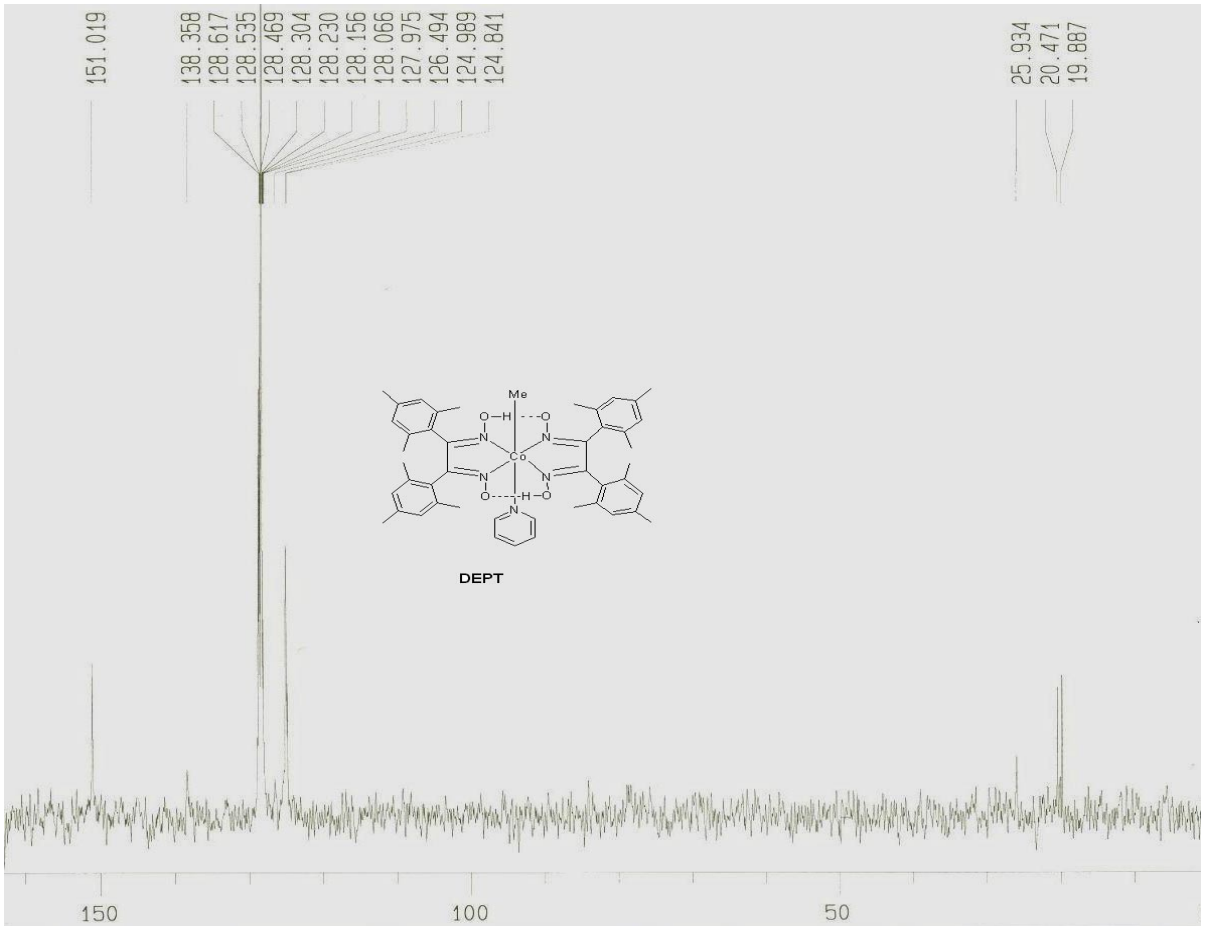

Fig. S5. DEPT spectrum of Compound **1.**

Fig S6. 400 MHz ^{1}H NMR of **ClCo(dmestgH)$_2$Py**

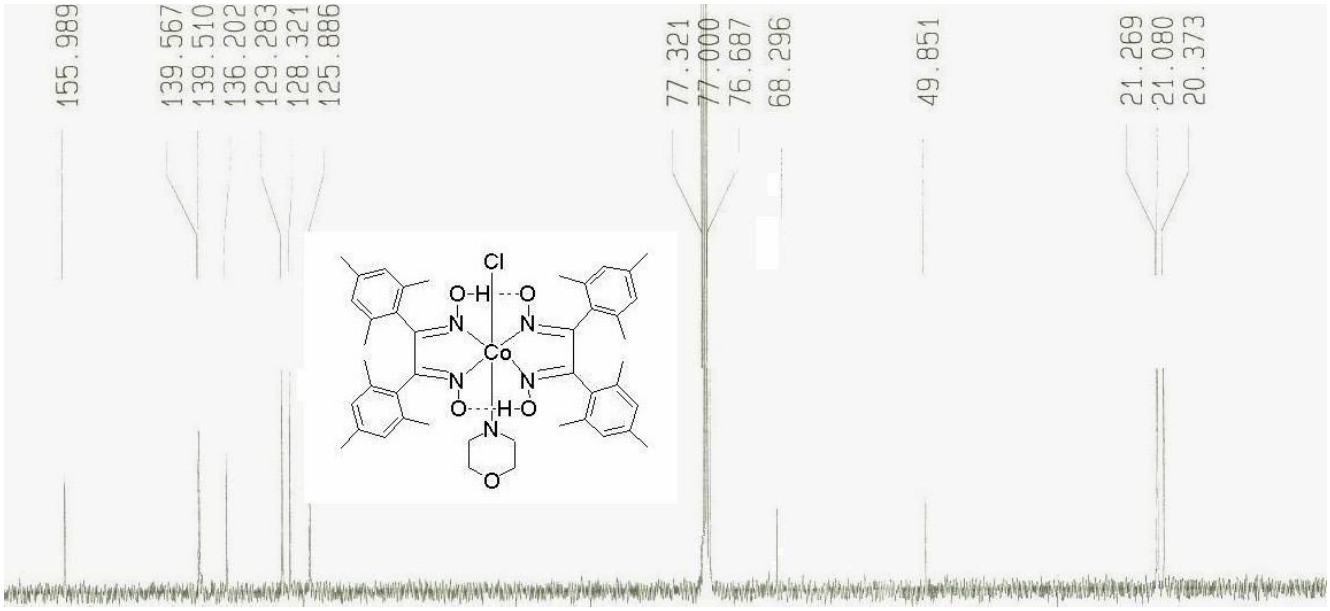

Fig S7. 100 MHz ^{13}C NMR of **ClCo(dmestgH)$_2$Py**

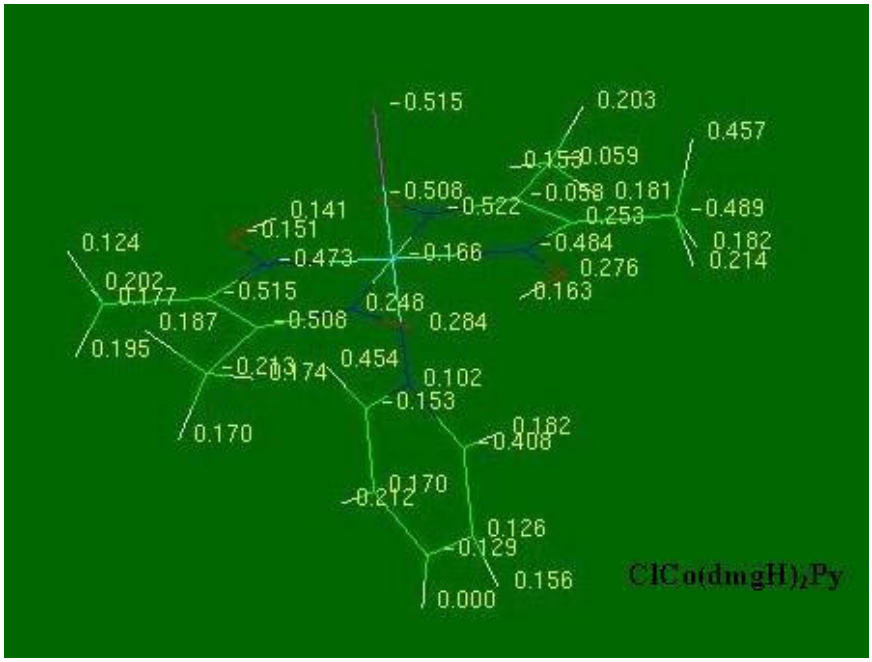

Fig S8. Charge density of $ClCo(dmgH)_2Py$ from ab. initio (DFT) calculation.

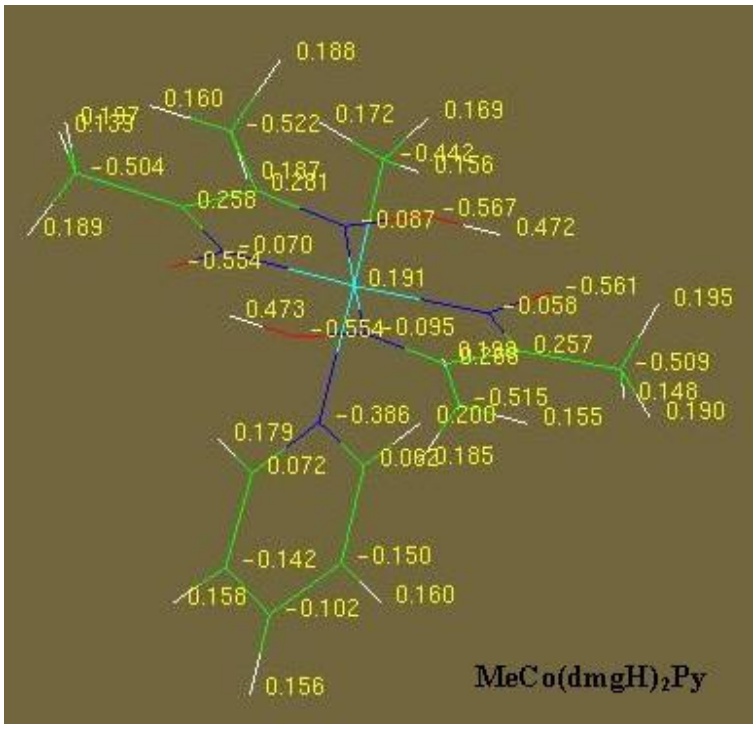

Fig S9. Charge density of $MeCo(dmgH)_2Py$ from ab. initio (DFT) calculation.

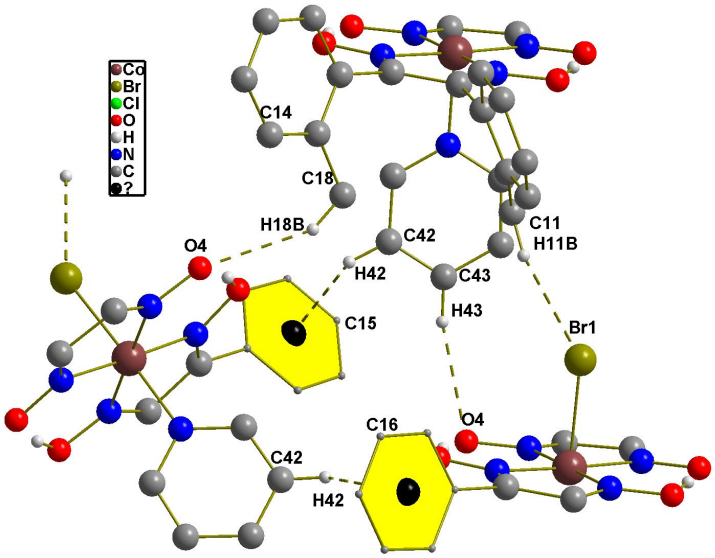

Fig 10. Showing the C-H…O and C-H… π interactions of **7**.

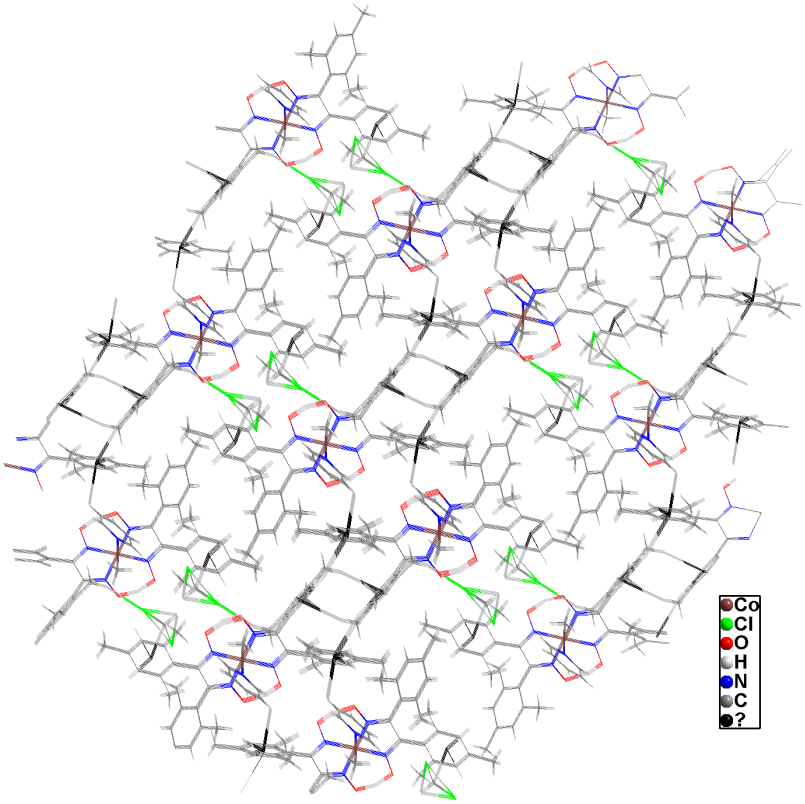

Fig 11. Showing two-dimensional array of **1** with the C-H…O and C-H… π interactions.