# Electronic Supplementary Information (ESI)

# The effect of remote substitution on formation of preferential isomers of cobalt(III)-tetrazolate complexes by microwave assisted cycloaddition

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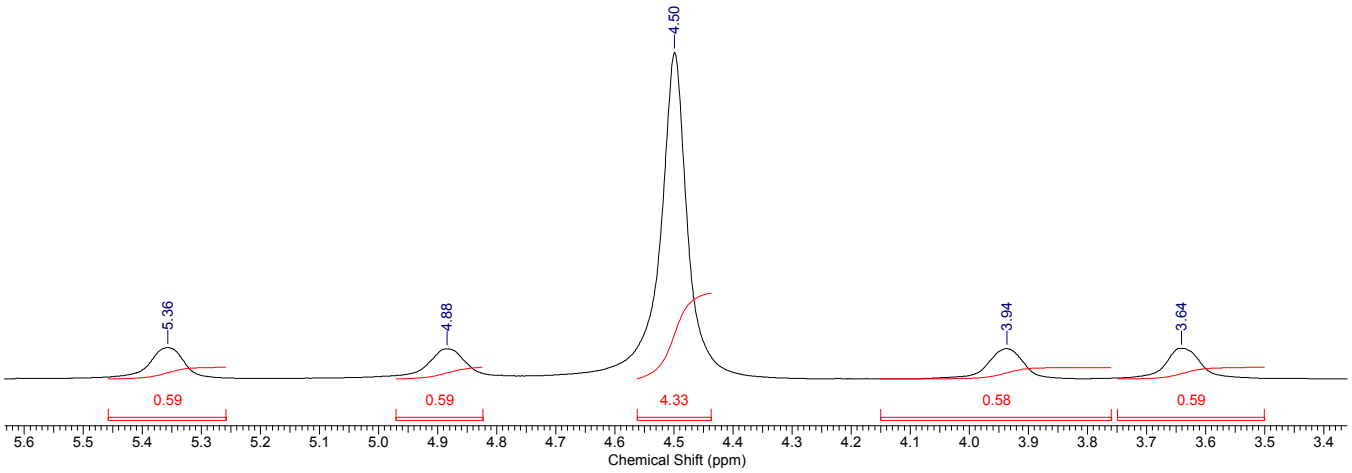



**Figure S1. $^{1}$H NMR Spectrum of mixture containing both *Cis*-2 and *Trans*-2.**

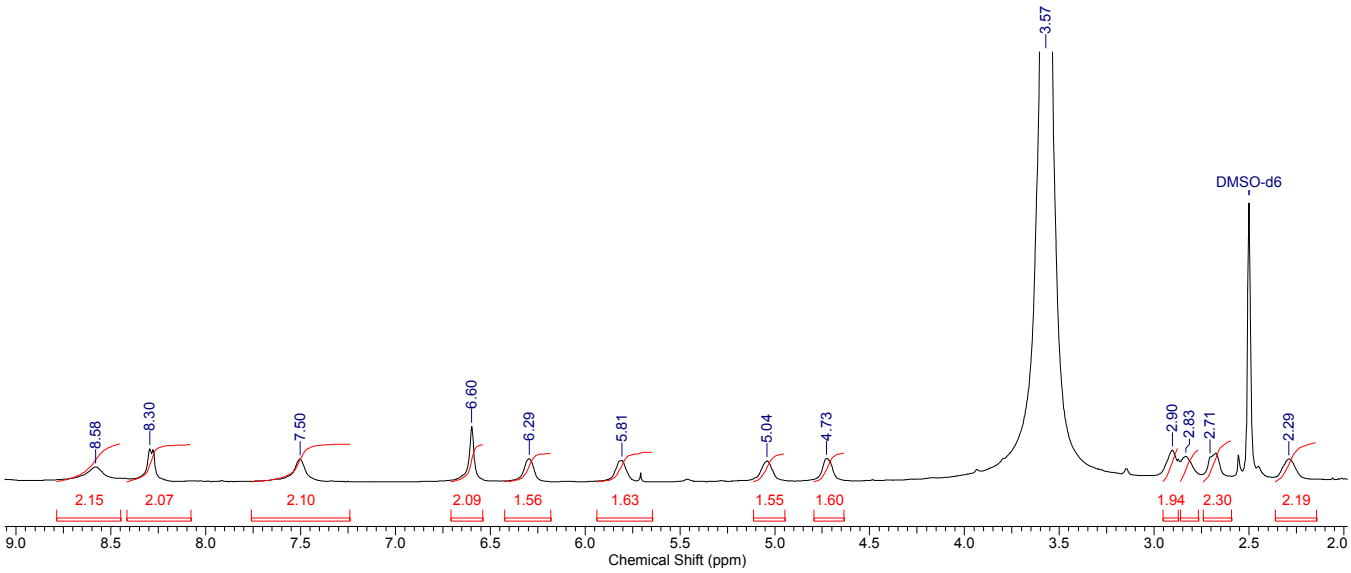



**Figure S2. $^{1}$H NMR Spectrum of *Cis*-2.**

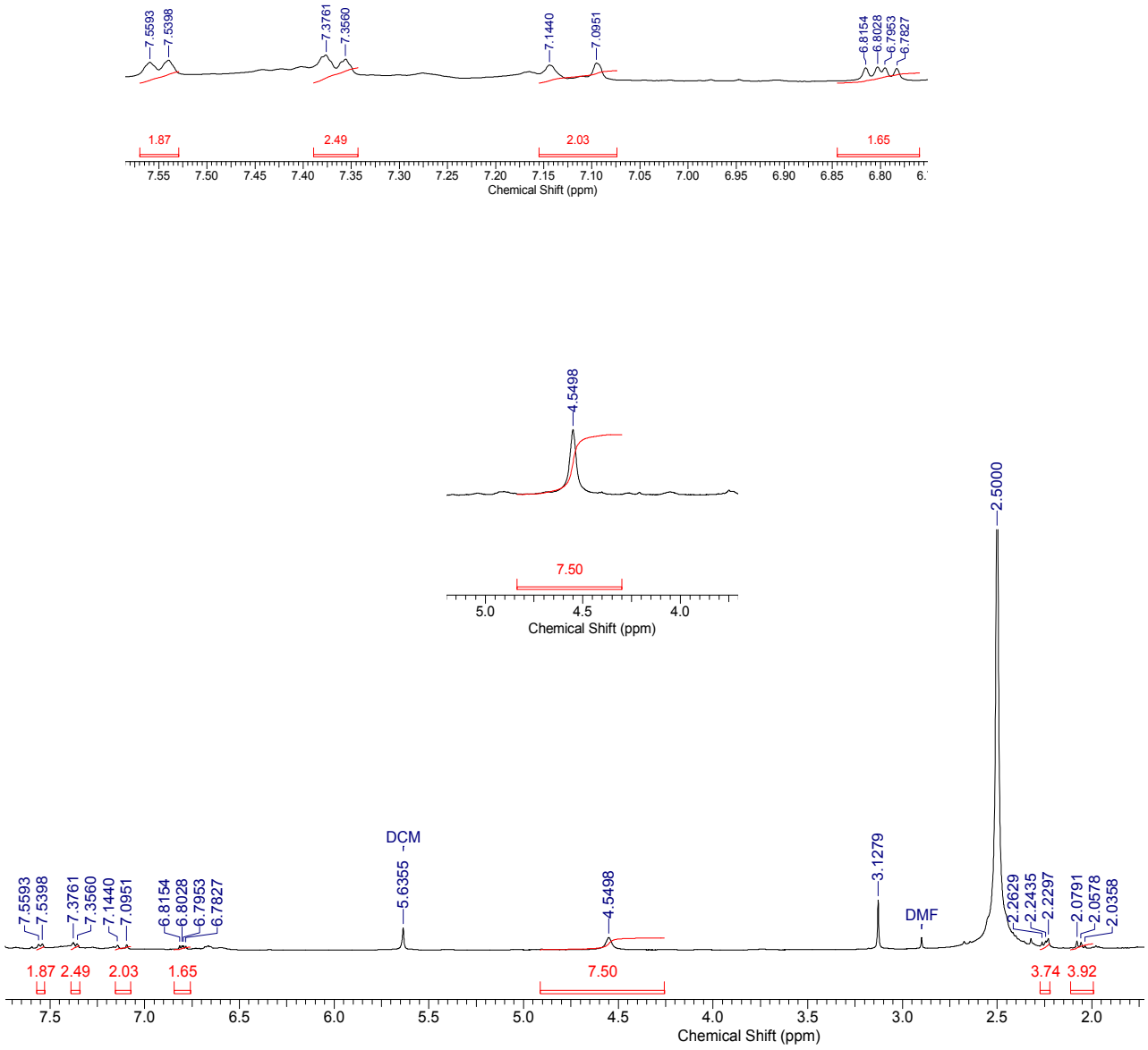



**Figure S3. $^{1}$H NMR Spectra of *Trans*-2.**

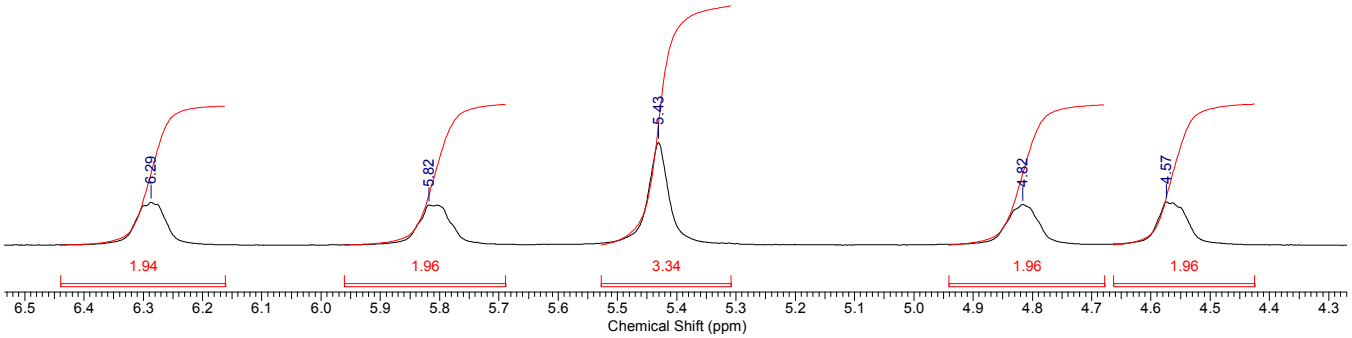



**Figure S4. $^{1}$H NMR Spectrum of mixture containing both *Cis*-5 and Trans-5.**

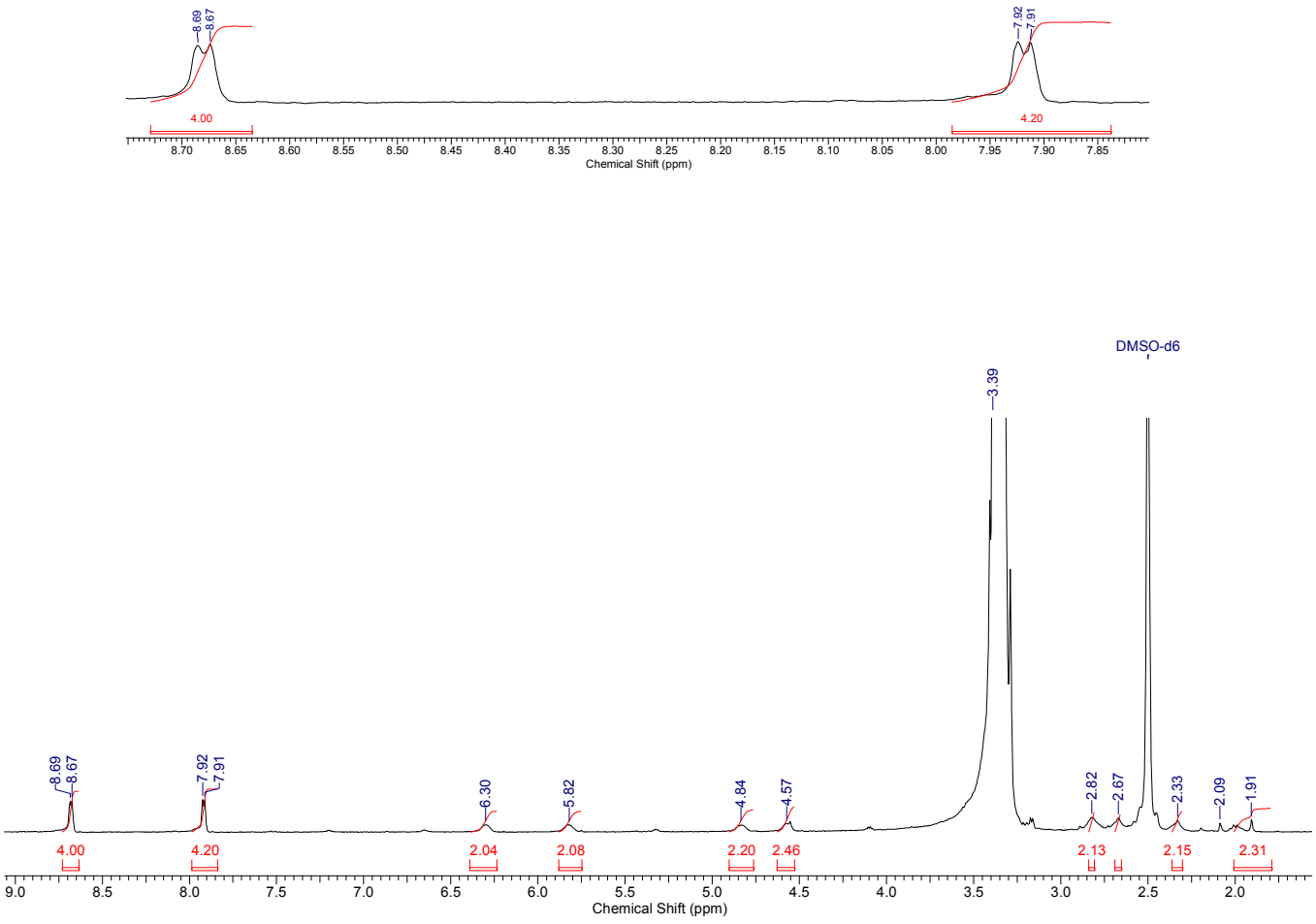



**Figure S5. $^{1}$H NMR Spectrum of *Cis*-5.**

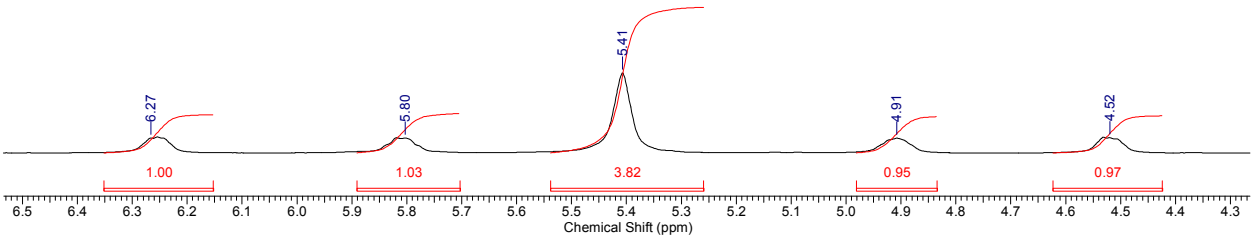
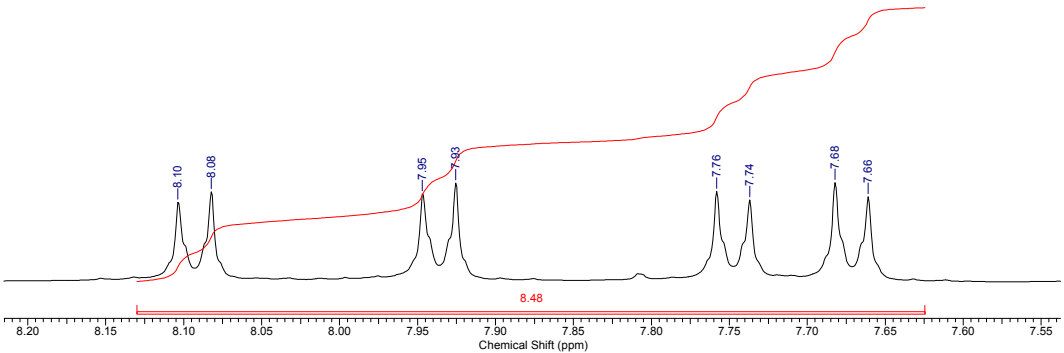



**Figure S6. 1H NMR Spectra of mixture containing both *Cis*-6 and Trans-6.**



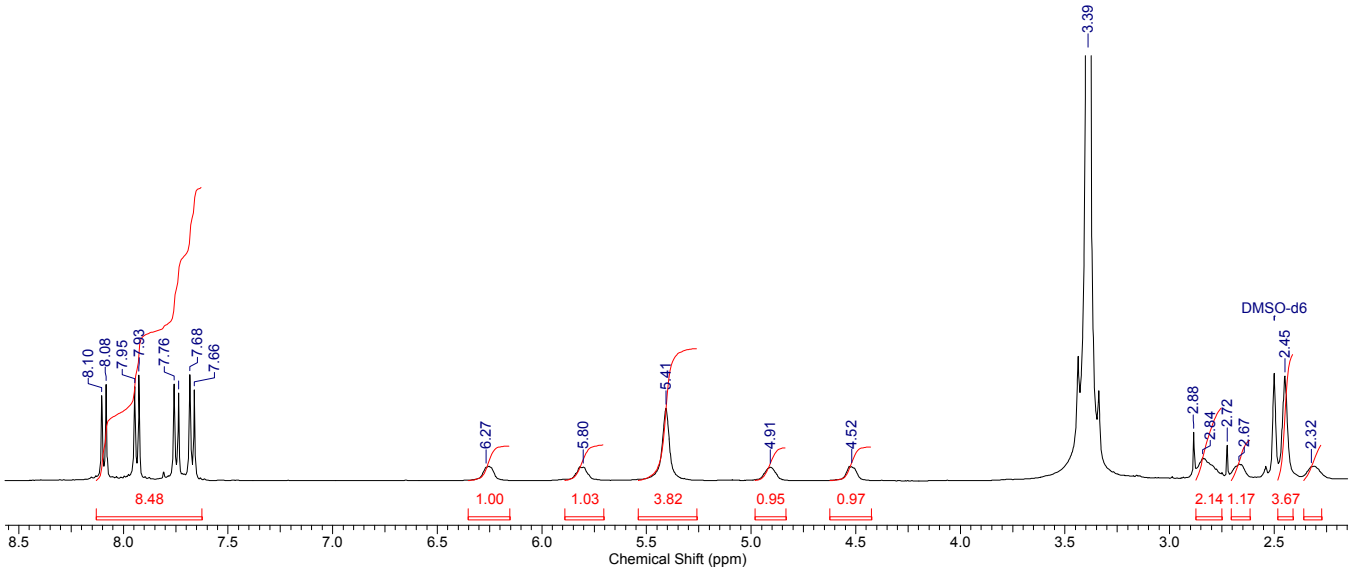



**Figure S7. 1H NMR Spectra of mixture containing both *Cis*-6 and Trans-6.**

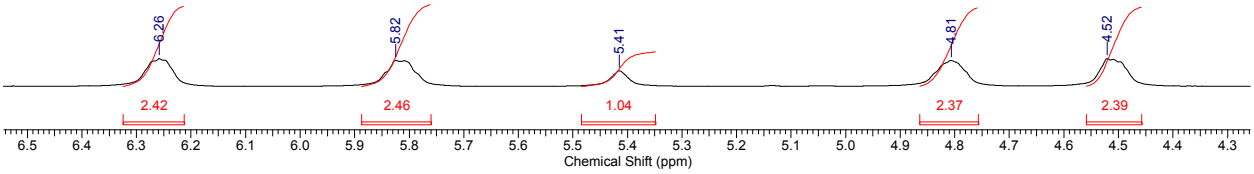
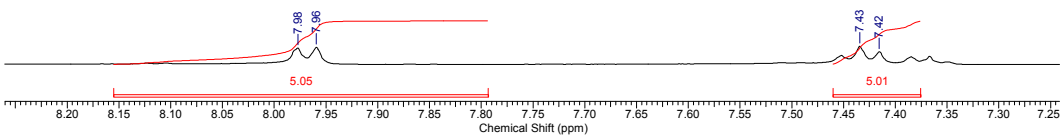



**Figure S8. 1H NMR Spectra of mixture containing both *Cis*-7 and Trans-7.**



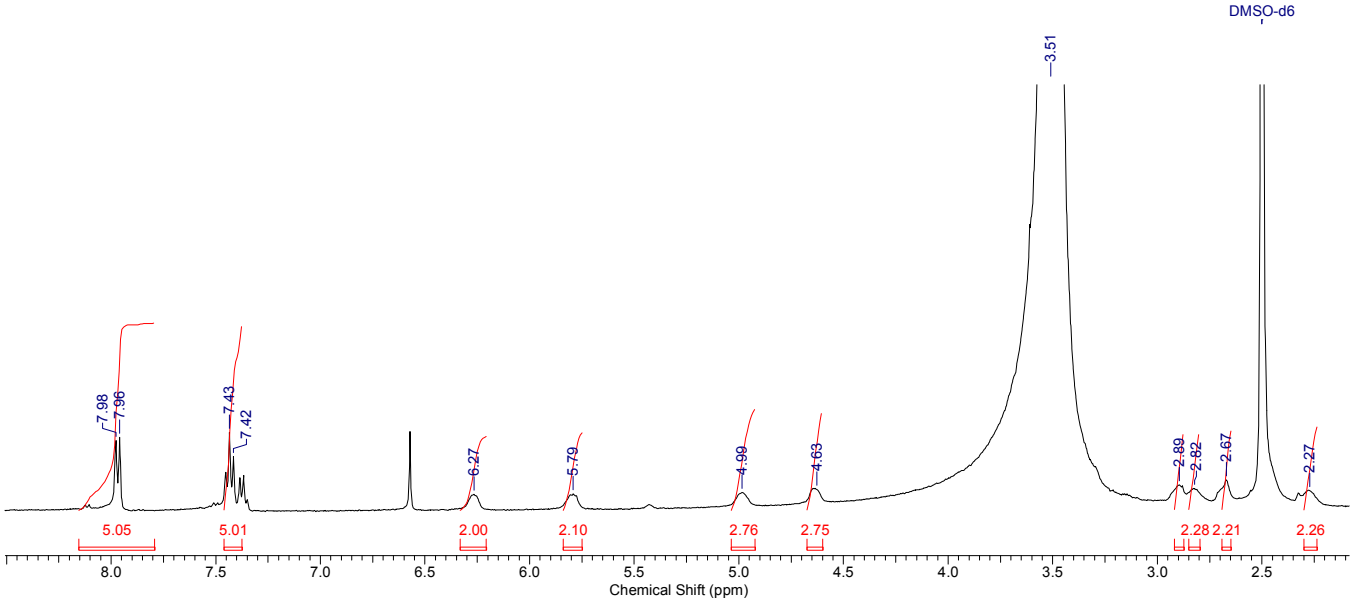



**Figure S9. 1H NMR Spectra of *Cis*-7.**

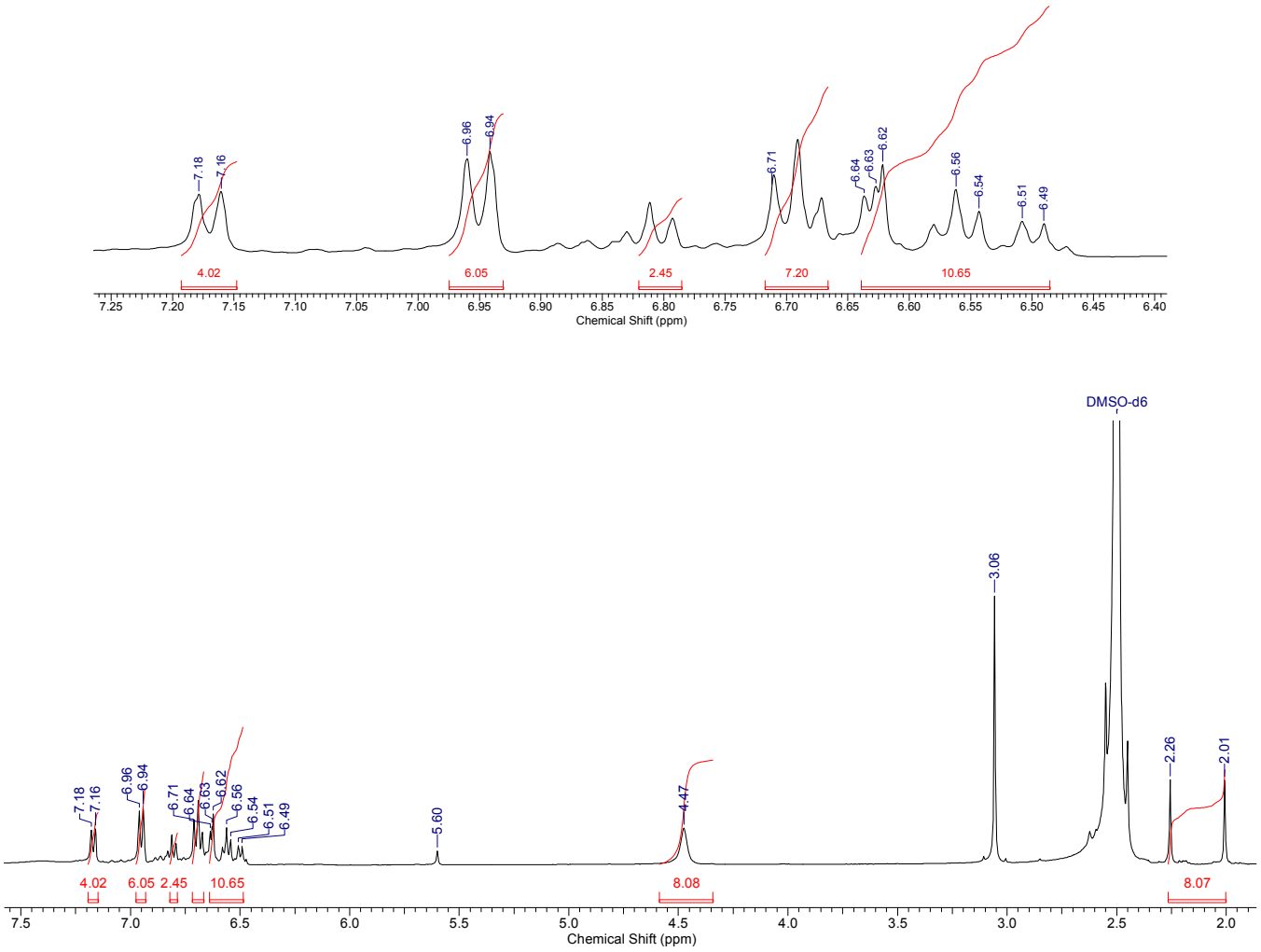



**Figure S10. 1H NMR Spectra of *Trans*-7.**

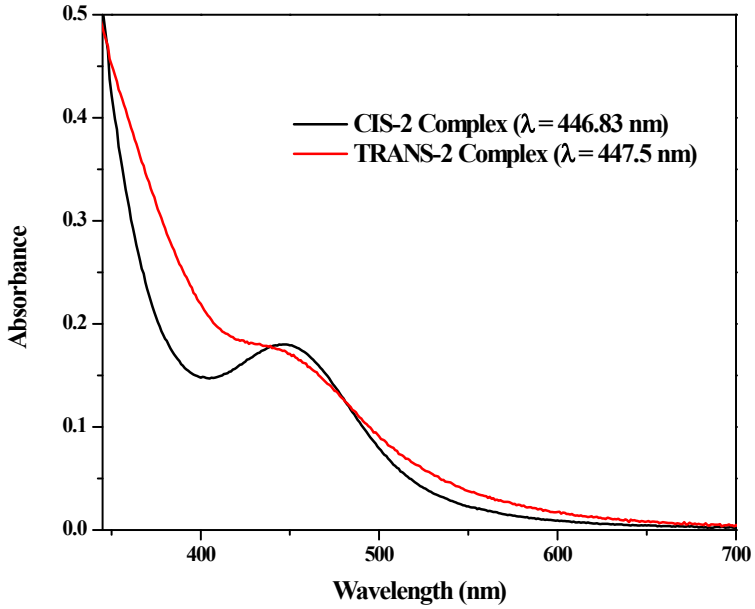



**Figure S11 : UV-vis spectra of compound *cis*-2 and *trans*-2**

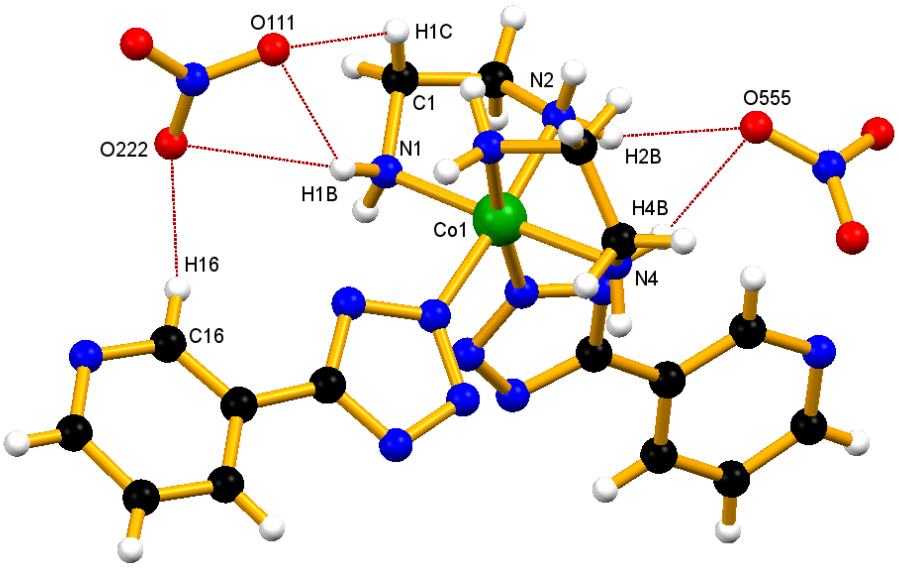



**Fig. S12a** Hydrogen-bonded interaction between complex molecule and nitrate ions in ***cis*-2**.

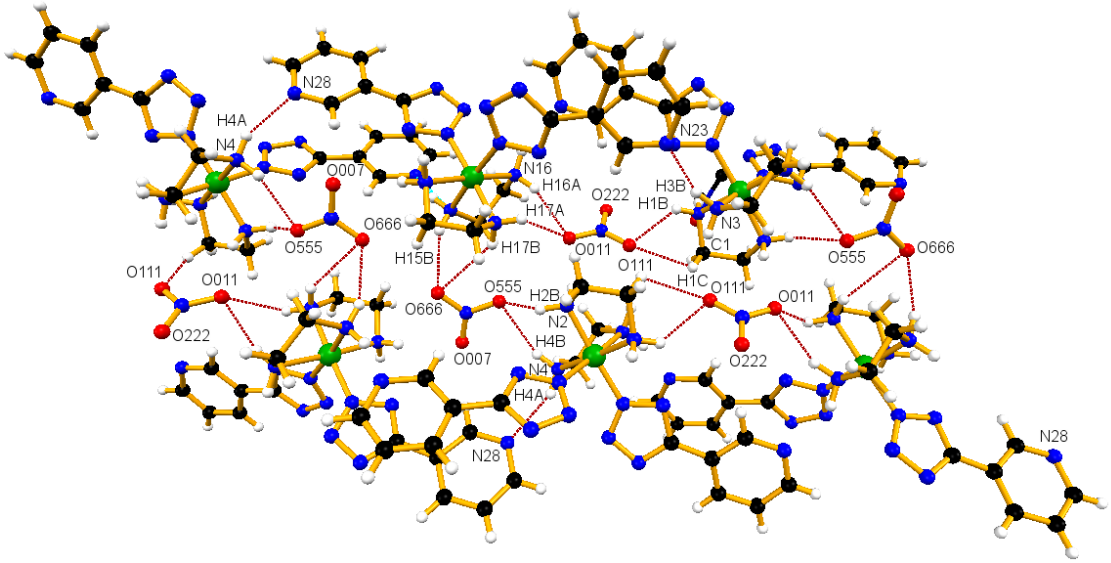



**Fig. S12b** Hydrogen bonding interaction between the ethylenediamine molecules and surrounding nitrate ions in ***cis*-2**.

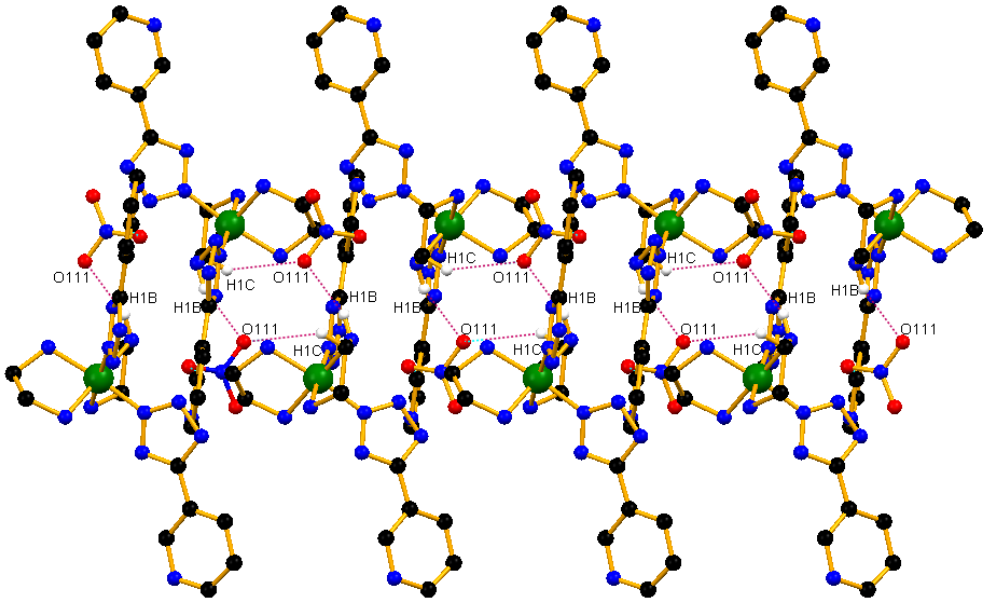



**Fig. S12c** Formation of hydrogen-bonded 1D polymer through the nitrate ions which bridges between the two crystallographically independent molecules in ***cis*-2**.

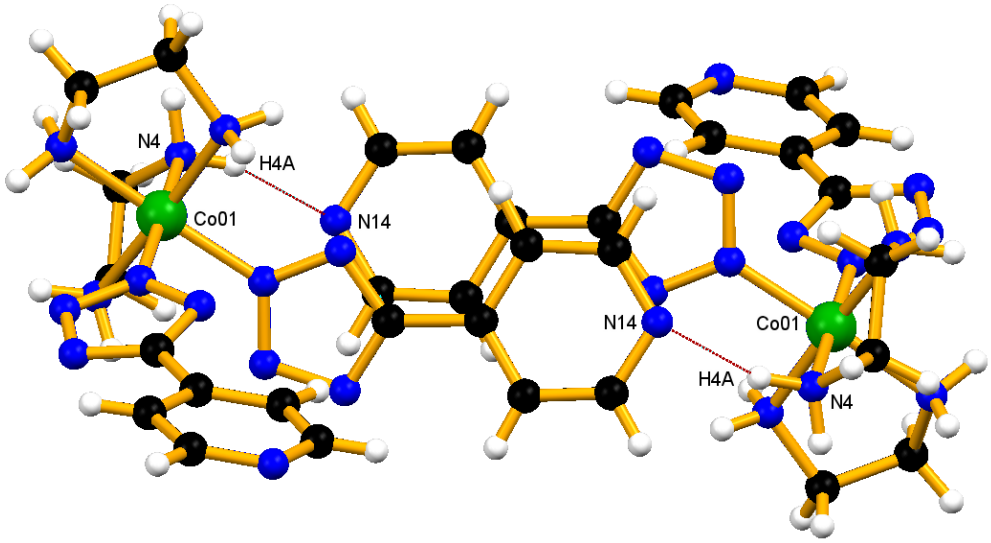



**Fig. S13a** Hydrogen bonded interaction between two molecules through pyridyl nitrogen in ***cis*-3**.

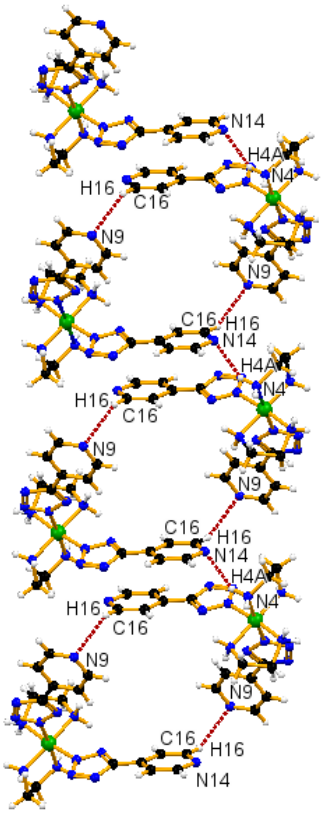



**Fig. S13b** Compound ***cis*-3** forms a ladder type of structure through hydrogen bonding along *c*-axis.

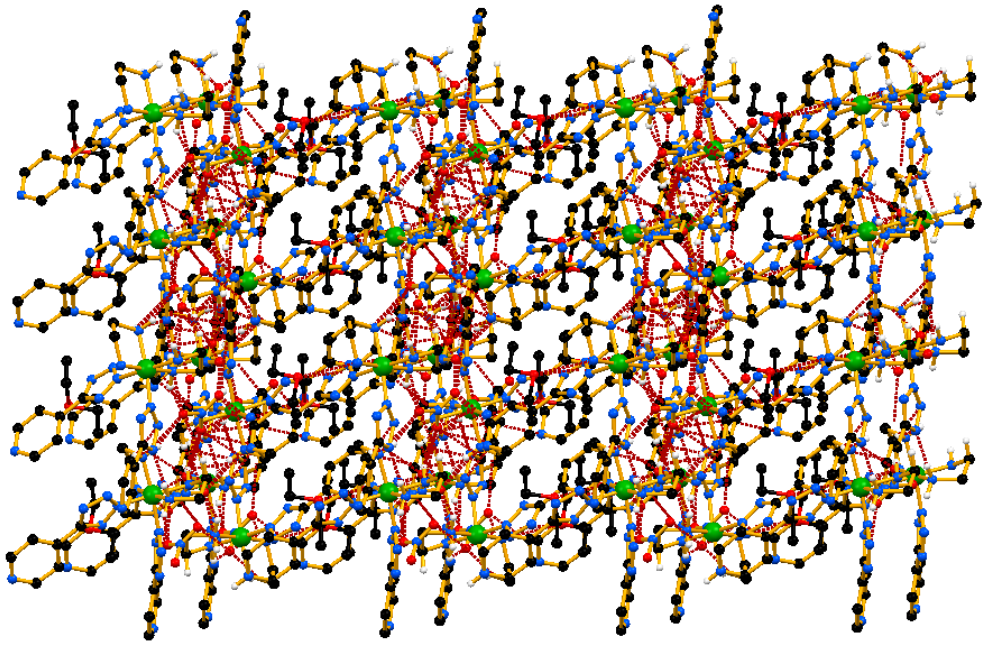


**Fig. S13c** Hydrogen bonded 3D structure of compound ***cis*-3**.

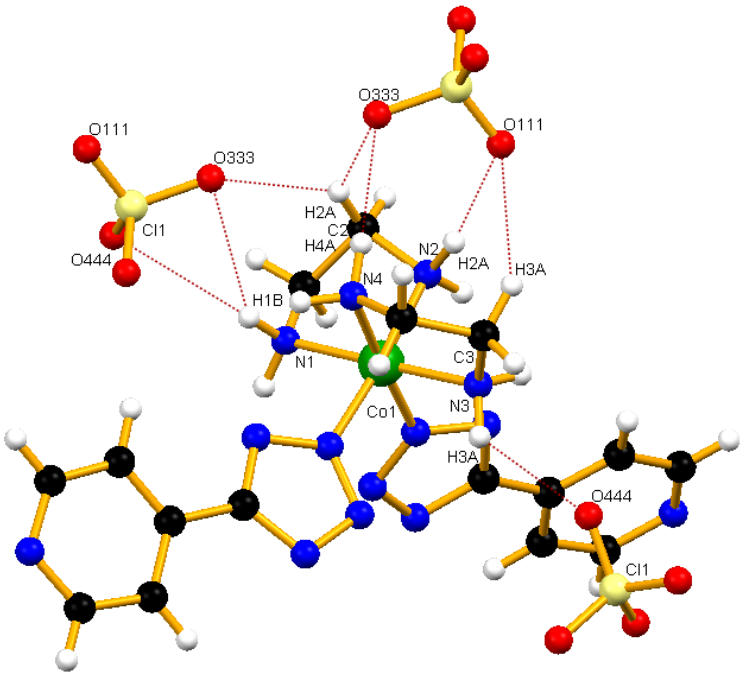



**Fig. S14a** The hydrogen bonded interactions between the complex and the surrounding perchlorate ions in ***cis*-5**.

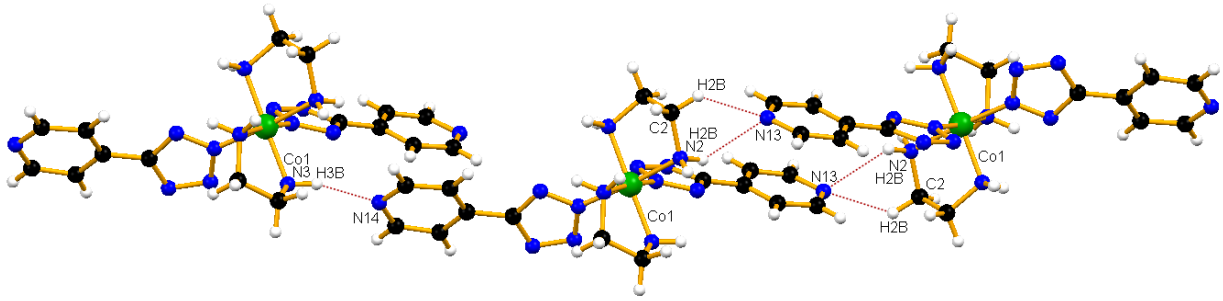



**Fig. S14b** Hydrogen bonded interaction between molecules through pyridyl nitrogen and ethylenediamine hydrogens in ***cis*-5**.

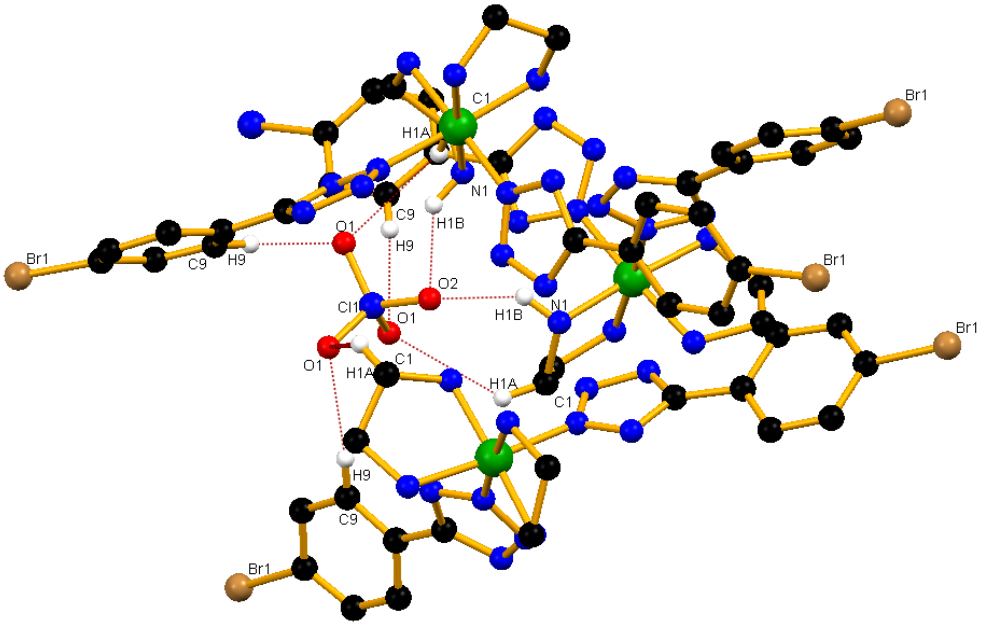



**Fig. S15a** Each perchlorate ions are connected with three molecules through three equivalent oxygen atom via hydrogen bonding interactions in compound ***cis*-6**.

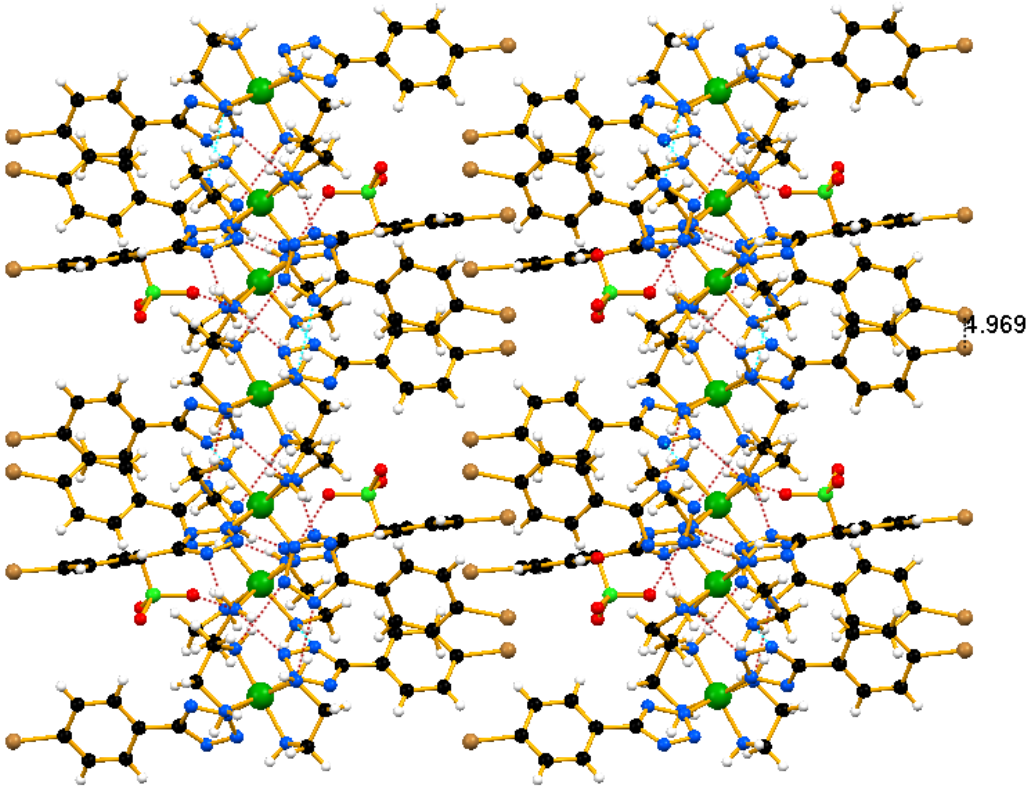



**Fig. S15b** 2D H-bonded packing network of compound ***cis*-6**.

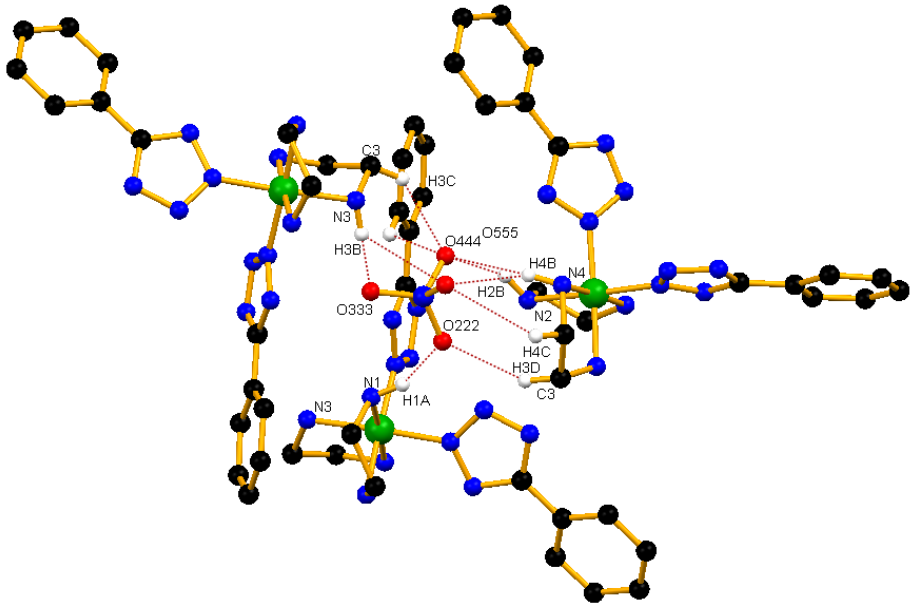



**Fig. S16a** Interactions between perchlorate ions with different molecules via hydrogen bonding in compound ***cis*-7**.

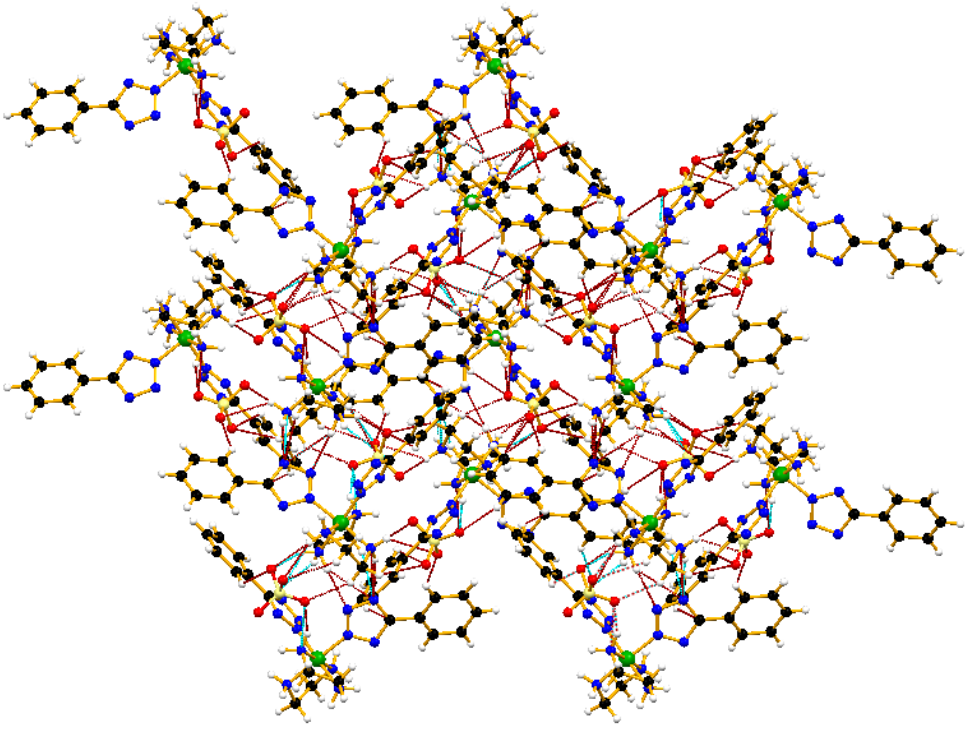


**Fig. S16b** Hydrogen bonded 3D network of compound ***cis*-7**.

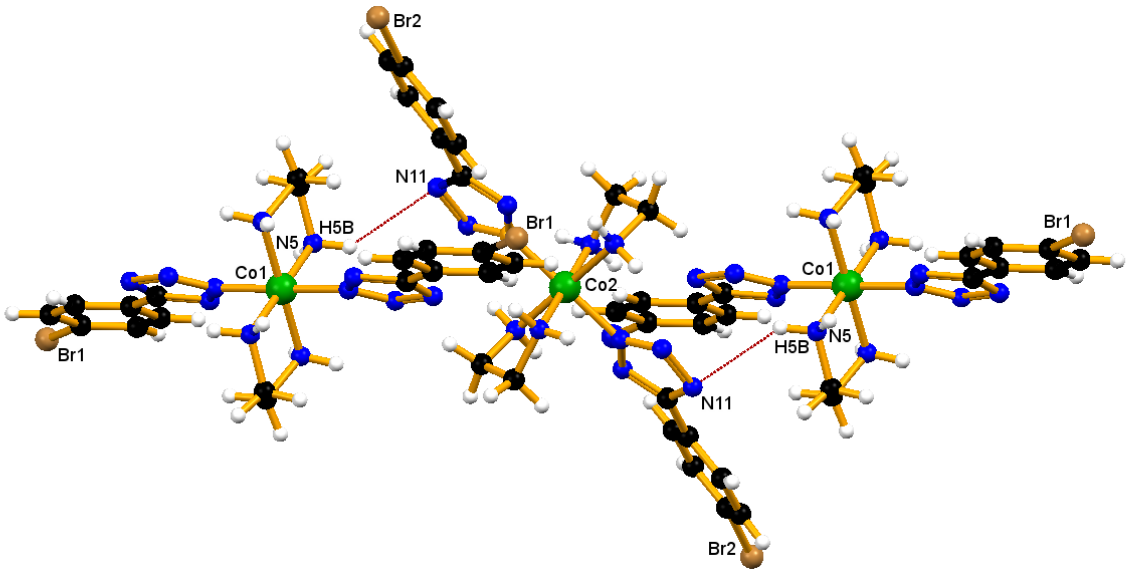



**Fig. S17a** H-bond formation between ethylenic hydrogen of one molecule and tetrazolyl nitrogen of the adjacent complex in ***trans*-4**.

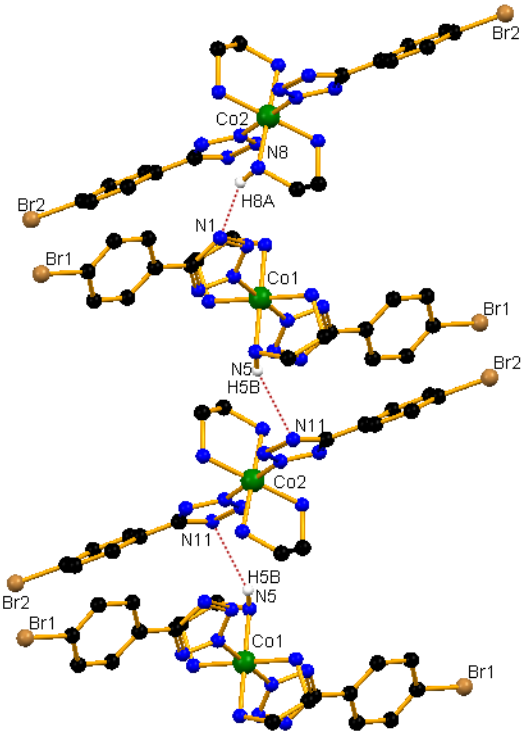



**Fig. S17b** View of 1D-chain along *b*-axis through H-bonding of ***trans*-4.**

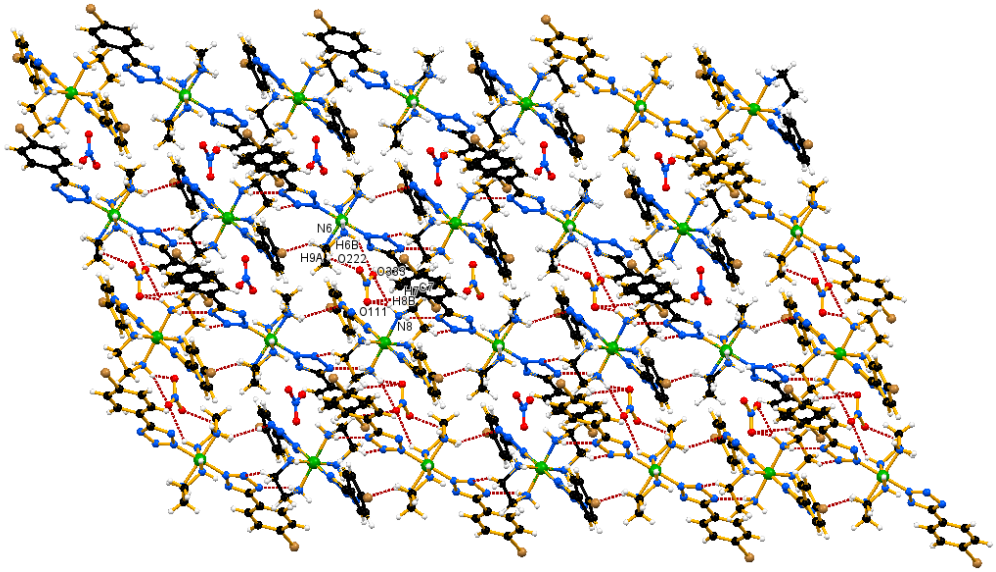



**Fig. S17c** Formation of 2D-network in *ab*-plane where nitrate ions connects with different molecules by hydrogen bonds in compound ***trans*-4**.

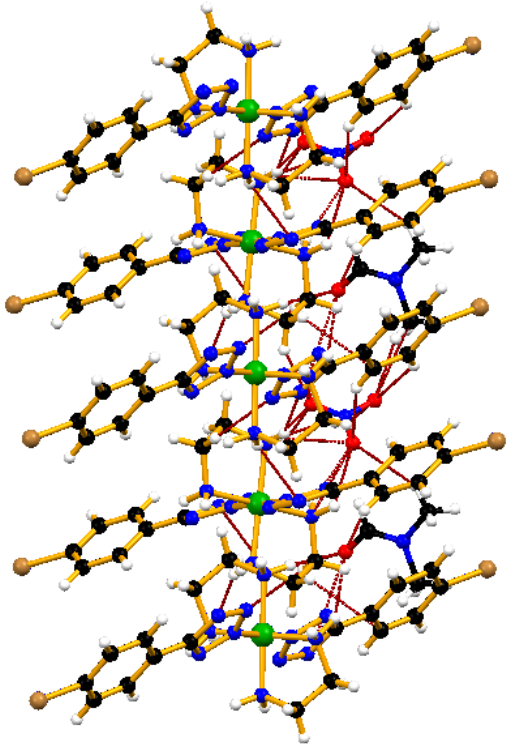


**Fig. S17d** Stacking of 5-substituted bromine atoms in compound ***trans*-4**.

**Table S1 :** Geometric features of internal hydrogen bonding interactions

**Table for compound *cis*-2:**

| D-H···A | d(D-H) / Å | d(H···A) / Å | d(D···A) / Å | ∠D-H···A / ° |
|---|---|---|---|---|
| N(2)-H(2B)···O(555) | 0.901 | 2.264 | 2.911 | 128.39 |
| N(1)-H(1B)···O(111) | 0.901 | 2.404 | 3.120 | 136.58 |
| C(1)-H1C···O(111) | 0.970 | 2.595 | 3.421 | 143.12 |
| N(16)-H(16)···O011 | 0.899 | 2.198 | 3.052 | 158.56 |
| N(17)-H(17A)···O011 | 0.901 | 2.377 | 3.002 | 126.60 |
| N(15)-H(15B)···O(666) | 0.900 | 2.273 | 3.108 | 154.24 |
| N(17)-H(17B)···O(666) | 0.900 | 2.655 | 3.388 | 139.30 |
| N(1)-H(1A)···O(888) | 0.901 | 2.346 | 3.065 | 136.75 |

**Table for compound *cis*-3:**

| D-H···A | d(D-H) / Å | d(H···A) / Å | d(D···A) / Å | ∠D-H···A / ° |
|---|---|---|---|---|
| N(1)-H(1A)···O(111) | 0.899 | 2.454 | 3.166 | 136.28 |
| N(4)-H(4B)···O(111) | 0.900 | 2.589 | 3.133 | 119.58 |
| N(1)-H(1A)···O(333) | 0.899 | 2.608 | 3.474 | 162.06 |
| N(4)-H(4A)···N(14) | 0.900 | 2.336 | 3.166 | 153.28 |
| C(16)-H(16)···N(9) | 0.930 | 2.742 | 3.547 | 145.40 |
| N(1)-H(1B)···O(101) | 0.900 | 2.258 | 3.033 | 144.09 |

**Table for compound *trans*-4 :**

| D-H···A | d(D-H) / Å | d(H···A) / Å | d(D···A) / Å | ∠D-H···A / ° |
|---|---|---|---|---|
| N(5)-H(5B)···N(11) | 0.900 | 2.622 | 3.362 | 140.08 |
| C(17A)-H17A···N(2) | 0.969 | 2.581 | 3.441 | 147.92 |
| N(8)-H(8A)···N(1) | 0.901 | 2.266 | 3.100 | 153.84 |
| C(7)-H(7)···O(111) | 0.930 | 2.626 | 3.405 | 141.75 |
| N(8)-H(8B)···O(111) | 0.900 | 2.593 | 3.201 | 125.54 |
| N(8)-H(8B)···O(333) | 0.900 | 2.010 | 3.163 | 158.20 |

**Table for compound *cis*-5 :**

| D-H···A | d(D-H) / Å | d(H···A) / Å | d(D···A) / Å | ∠D-H···A / ° |
|---|---|---|---|---|
| N(1)-H1B···O(444) | 0.920 | 2.695 | 3.497 | 138.36 |
| N(1)-H(1B)···O(333) | 0.920 | 2.638 | 3.399 | 140.62 |
| C(2)-H(2A)···O(333) | 0.989 | 2.672 | 3.490 | 140.23 |
| N(4)-H(4A)···O(333) | 0.920 | 2.209 | 3.113 | 167.22 |
| N(2)-H(2A)···O(111) | 0.920 | 2.176 | 3.076 | 165.81 |
| C(3)-H(3A)···O(111) | 0.990 | 2.701 | 3.560 | 145.35 |
| N(3)-H(3A)···O(444) | 0.920 | 2.450 | 3.122 | 129.97 |
| N(3)-H(3B)···N(14) | 0.920 | 2.088 | 2.949 | 155.35 |
| N(2)-H(2B)···N(13) | 0.920 | 2.471 | 3.194 | 135.62 |
| C(2)-H(2B)···N(13) | 0.991 | 2.679 | 3.317 | 122.41 |

**Table for compound *cis*-6 :**

| D-H···A | d(D-H) / Å | d(H···A) / Å | d(D···A) / Å | ∠D-H···A / ° |
|---|---|---|---|---|
| C(9)-H9···O(1) | 0.929 | 2.653 | 3.580 | 174.77 |
| N(1)-H(1B)···O(2) | 0.899 | 2.325 | 2.986 | 130.24 |
| C(1)-H(1A)···O(1) | 0.970 | 2.715 | 3.401 | 128.06 |

**Table for compound *cis*-7 :**

| D-H···A | d(D-H) / Å | d(H···A) / Å | d(D···A) / Å | ∠D-H···A / ° |
|---|---|---|---|---|
| N(1)-H1A···O(222) | 0.920 | 2.209 | 3.010 | 145.23 |
| C(17)-H(17)···O(222) | 0.951 | 2.590 | 3.512 | 163.67 |
| C(7)-H(7)···O(444) | 0.949 | 2.698 | 3.349 | 126.37 |
| C(14)-H(14)···O(555) | 0.950 | 2.602 | 3.394 | 141.11 |
| C(3)-H(3C)···O(444) | 0.990 | 2.676 | 3.541 | 146.12 |
| N(4)-H(4B)···O(555) | 0.920 | 2.662 | 3.362 | 133.55 |
| N(2)-H(2B)···O(444) | 0.920 | 2.426 | 3.217 | 144.12 |