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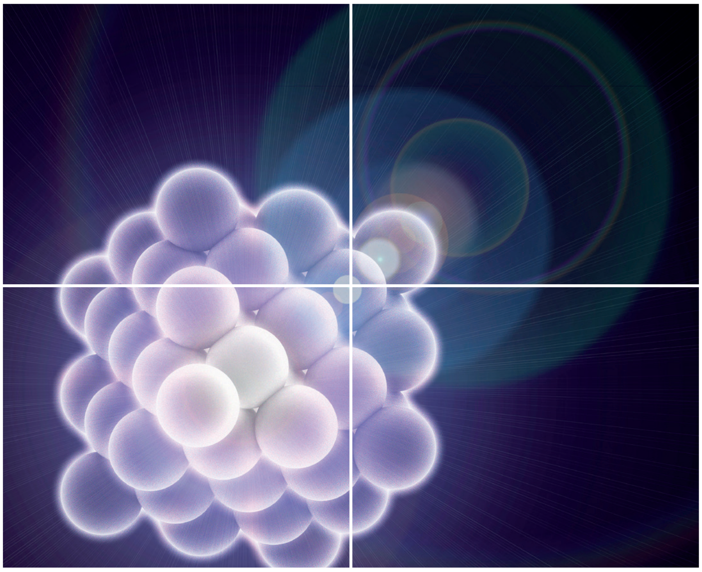

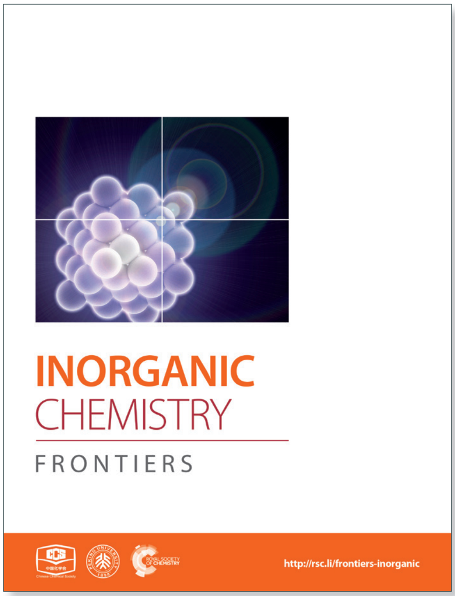

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The effect of remote substitution on formation of preferential isomers of cobalt(III)-tetrazolate complexes by microwave assisted cycloaddition

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*ESI   *Electronic Supplementary Information*

Abstract

1,3-dipolar cycloaddition reaction of *cis*-[Co(N_3)$_2$(en)$_2$]NO_3 **1** with different organonitriles NCR under focussed microwave irradiation produced *bis*-tetrazolate complexes [Co(N_4CR)$_2$(en)$_2$](NO_3). Interestingly in the case of 3-cyano pyridine the reaction produced both *cis*- and *trans*-isomers (***cis*-2** and ***trans*-2**), whereas for 4-cyano pyridine the compound obtained was exclusively *cis*- (***cis*-3**) and for 4-bromobenzonitrile it was only *trans*- (***trans*-4**) compound which was isolated. This indicates a probable role of remote substitution in phenyl ring which dictates the formation of preferential isomer. When started from the *trans*-variety of the diazido complex *trans*-[Co(N_3)$_2$(en)$_2$]ClO_4 **1a**, upon reacting with the same or other nitriles it produced a mixture of *cis*- and *trans*- isomers of [Co(N_4CR)$_2$(en)$_2$]ClO_4 in all the cases with a more preference towards *cis*- geometry [R = 4-NC_5H_4 (***cis*-5 and *trans*-5**), 4-BrC_6H_4 (***cis*-6 and *trans*-6**) and C_6H_5(***cis*-7** and ***trans*-7**)]. The preferential formation of *cis*-analogue of compound *trans*-**4** starting from *trans*-precursor was quite curious. A theoretical

investigation between compound ***trans*-4** and ***cis*-6** reveals that the extra stability of *trans*-complex **4** may be arising out of additional van der Waals interaction in the solid state because of the presence of an extra DMF molecule as solvent of crystallization. However, an interactive counter-anion and a probable halogen-halogen interaction may also contribute in the formation of preferential isomers for cycloadded complexes even in the solution state.

Introduction

Metal promoted azidation of nitriles provides an easy and convenient method to synthesize metal tetrazolate complexes. Tetrazole behaves as an interesting ligand as it can act in a unidentate or polydentate fashion furnishing mono- and polynuclear compounds with interesting topologies.[1] Moreover tetrazole based complexes evoked much interests because of its utility in organic synthesis,[2] gas generating agent,[3] medicinal chemistry[4] and anti-corrosion species.[5] In recent past many metal tetrazolate complexes have been synthesized by [2 + 3] cycloaddition of metal ligated azide and nitriles. However, most of them are associated with group 10 transition metals[6] apart from some limited examples of some other transition elements.[7,8] Though there are few examples of cobalt tetrazolate complexes, however in most of the cases the tetrazole itself has been used as the ligand[9,10] or it has been generated by *in situ* [2 +3] cycloaddition of azide and nitrile in a hydrothermal process.[11] To the best of our knowledge there are very few examples where *in-situ* generation of tetrazolate ligand has been reported using cobalt ion in a controlled and systematic manner.[12,13] Moreover, as cobalt(III) ion tends to form different geometrical isomers it was also interesting to investigate if there is any influence of the counter-ions used and remote substitution of 5-tetrazole ligands on the overall preferential geometry adopted by the cobalt center.

Herein, we have investigated the reactions of different organonitriles with cobalt(III) coordinated azides and found that *cis*-[Co$(N_3)_2$$(en)_2$]$NO_3$ and *trans*-[Co$(N_3)_2$$(en)_2$]$ClO_4$ react with various RCN to give corresponding *cis*- or *trans*-bis(tetrazolate) complexes or their mixtures depending upon various factors like remote substitution, counter-anion used or solvent of crystallization in the cycloadded tetrazolato ligand.

Experimental Section

Materials and Instrumentations

All the chemical reagents required were purchased from sigma and used without further purification. *Cis*-[Co$(N_3)_2$$(en)_2$]$(NO_3)$ **1** and *trans*-[Co$(N_3)_2$$(en)_2$]$(ClO_4)$ **1a** were prepared according to reported methods.[14] Infrared spectra (4000–500 cm^{-1}) were recorded with a BRUKER TENSOR 27 instrument in KBr pellets. Mass spectrometric analyses had done on Bruker-Daltonics, microTOF-Q II mass spectrometer and the microwave irradiation experiments had done in focused microwave CEM discover reactor 300W and the reaction tube used was with 10ml capacity and 13mm internal diameter. Elemental analyses were carried out with a ThermoFlash 2000 elemental analyzer. UV-visible absorption spectra of all the compounds in methanol were recorded on a Carry-100 Bio UV-Visible spectrophotometer. ^1H NMR (400 MHz) in DMSO-d_6 were measured on a AVANCE III 400 Ascend Bruker BioSpin machine at ambient temperature.

Caution! *Azide, tetrazolate and perchlorate compounds are potentially explosive. Only a small amount of material should be prepared and handled with care.*

Synthesis

***cis*-[Co{5-(3-pyridyl)-tetrazolato}$_2$$(en)_2$]$NO_3$.DMF (*cis*-2) and trans-[Co{5-(3-pyridyl)-tetrazolato}$_2$$(en)_2$]$NO_3$ (*trans*-2) :** 0.12 g (0.37 mmol) of cobalt diazide complex **1** was dissolved in 5 mL of DMF in a cylindrical pyrex tube and 0.31 g (3 mmol) of 3-cyanopyridine was added to that solution. The system was irradiated for 1 h at 130 ° C in microwave reactor. The solvent was then removed *in vacuo* and the resulting reddish-brown residue was washed several times with diethyl ether to obtain a brown powder. The presence of both *cis*- and *trans*-isomer was detected in the resultant compound by ^{1}H NMR spectroscopy which are formed tentatively in 1:4 ratio (**Figure S1: ESI)**. The mixture was separated by ion-exchange chromatography using SP-Sephadex C-25 which is a strongly acidic ($-SO_3^-Na^+$) cation exchanger based on cross-linked dextran. 0.1 (M) $NaNO_3$ solution was used as the elution solvent to run the column. Both the isomers were further recrystallized from DMF/diethyl ether mixture. Though it was possible to grow suitable X-ray diffraction quality crystals for compound ***cis*-2** during recrystallization, however no single crystal was obtained for the corresponding *trans* variety.

***cis*-[Co{5-(3-pyridyl)-tetrazolato}$_2$(en)$_2$]NO$_3$.DMF (*cis*-2) :** Yield: 11% IR (KBr, cm^{-1}): $\nu_{C=N}$ 1640. NO_3 1384 Anal. Calc. for $C_{19}H_{24}N_{16}O_4Co$ (599.43) :C 38.03; H 4.00; N 37.36; Found : C 37.92; H 3.89; N 37.20; MS(ESI): m/z = 471.15 [M]$^+$. ^{1}H NMR :δ_H (400 MHz, DMSO- *d*$_6$, Me_4Si): 2.29-2.90 (m,8H,CH_2), 4.73 (s, 2H, NH_2), 5.04 (s, 2H, NH_2), 5.81 (s, 2H, NH_2), 6.29 (s, 2H, NH_2), 6.60 (s, 2H, aromatic), 7.50 (s, 2H,aromatic), 8.30 (s, 2H, aromatic), 8.58 (s, 2H, aromatic) ; (Figure S2: ESI for ^{1}H NMR spectra).

***trans*-[Co{5-(3-pyridyl)-tetrazolato}$_2$(en)$_2$]NO$_3$.DMF (*trans*-2) :** Yield: 38% IR (KBr, cm^{-1}): $\nu_{C=N}$ 1617. NO_3 1384 Anal. Calc. for $C_{19}H_{24}N_{16}O_4Co$ (599.43) :C 38.03; H 4.00; N 37.36; Found : C 37.83; H 3.82; N 37.03; MS(ESI): m/z = 471.15 [M]$^+$. ^{1}H NMR :δ_H (400 MHz, DMSO- *d*$_6$, Me_4Si): 2.06-2.26 (m,8H,CH_2), 4.55 (s, 8H, NH_2), 6.78-7.55 (m, 8H, aromatic); (Figure S3: ESI for ^{1}H NMR spectra).

***cis*-[Co{5-(4-pyridyl)-tetrazolato}$_2$(en)$_2$]NO$_3$.Et$_2$O (*cis*-3) :**

This compound was prepared in an identical manner which has been followed for compound ***cis*-2**. However, in this case the only pure *cis*-compound has been isolated instead of a mixture and it was recrystallized from methanol/diethyl ether mixture which produced some single crystals for X-ray diffraction analysis.

***cis*-[Co{5-(4-pyridyl)-tetrazolato}$_2$(en)$_2$]NO$_3$.Et$_2$O (*cis*-3) :** Yield: 58% IR (KBr, cm^{-1}): $\nu_{C=N}$ 1614. NO$_3$ 1384 Anal. Calc. for $C_{20}H_{24}N_{15}O_4Co$ (597.47) :C 40.16; H 4.01; N 35.14; Found : C 39.94; H 3.89; N 35.04; MS(ESI): m/z = 471.20 [M]$^+$**.** ^{1}H NMR :δ_H (400 MHz, DMSO- *d*$_6$, Me$_4$Si): 2.34-2.83 (m,8H,CH$_2$), 4.60 (s, 2H, NH$_2$), 4.85 (s, 2H, NH$_2$), 5.82 (s, 2H, NH$_2$), 6.31 (s, 2H, NH$_2$), 7.91 (d, 4H, aromatic), 8.87 (d, 4H, aromatic); (Figure 1 for ^{1}H NMR spectra).

***trans*-[Co{5-(4-bromophenyl)-tetrazolato}$_2$(en)$_2$]NO$_3$.DMF (*trans*-4) :**

A solution of 0.12 g (0.37 mmol) of cobalt diazide complex **1** and 0.54 (3 mmol) of 4-bromobenzonitrile in 5 mL of DMF was taken in a cylindrical pyrex tube and it was irradiated for 3 hrs at 130 ° C. The solvent was then removed *in vacuo* and the resulting reddish-brown residue was washed several times with diethyl ether to obtain a brown powder which was then recrystallized from DMF/ether mixture to obtain reddish-brown crystalline compound along with single crystals suitable for X-ray diffraction studies.

***trans*-[Co{5-(4-bromophenyl)-tetrazolato}$_2$(en)$_2$]NO$_3$.DMF (*trans*-4) :** Yield: 56% IR (KBr, cm^{-1}): $\nu_{C=N}$ 1665. NO$_3$ 1384. Anal. Calc. for $C_{21}H_{31}N_{14}O_4Br_2Co$ (762.35) :C 33.05; H 4.06; N 25.70; Found : C 32.85; H 3.90; N 25.31; MS(ESI): m/z = 626.99 [M]$^+$. ^{1}H NMR :δ_H (400 MHz, DMSO- *d*$_6$, Me$_4$Si): 2.45 (s, 8H, CH$_2$), 5.41 (s, 8H, NH$_2$), 7.73 (d, 4H, aromatic), 8.08 (d, 4H, aromatic); (Figure 2 for ^{1}H NMR spectra).

***cis*-[Co{5-(4-pyridyl)-tetrazolato}$_2$(en)$_2$]ClO$_4$.H$_2$O (*cis*-5)** 0.12 g (0.33 mmol) of *trans*-cobalt diazide complex **1a** was dissolved in 5 mL of DMF in a cylindrical pyrex tube and 0.31 g (3 mmol) of 4-cyanopyridine was added to that solution. The system was irradiated for 1 h at 130 °C in microwave reactor. The solvent was then removed *in vacuo* and the resulting reddish-brown residue was washed several times with diethyl ether to obtain a brown powder. This brown powder was found to be a mixture of *cis*- and *trans*-[Co{5-(4-pyridyl)-tetrazolato}$_2$(en)$_2$]ClO$_4$ which was formed tentatively in 5:2 ratio (Figure S4: ESI for ^{1}H NMR spectra**)**. The mixture was tried to be separated by ion-exchange method through SP-Sephadex C-25. However, only *cis*- compound could have been isolated upon elution with NaNO$_3$ whereas the *trans*-compound gets decomposed in ion-exchange resin column. The resultant *cis*-compound was then recrystallized from methanol/diethyl ether mixture which furnished some X-ray diffraction quality crystals.

***cis*-[Co{5-(4-pyridyl)-tetrazolato}$_2$(en)$_2$]ClO$_4$.H$_2$O (*cis*-5) :** Yield: 56% IR (KBr, cm^{-1}): $\nu_{C=N}$ 1612. ClO$_4$ 1096. Anal. Calc. for $C_{16}H_{26}N_{14}O_5CoCl$ (588.85) :C 32.60; H 4.41; N 33.28; Found : C 32.06; H 4.10; N 33.07; MS(ESI): m/z = 471.15 [M]$^+$. ^{1}H NMR :δ_H (400 MHz, DMSO- d_6, Me$_4$Si): 1.91-2.82 (m,8H,CH$_2$), 4.57 (s, 2H, NH$_2$), 4.84 (s, 2H, NH$_2$), 5.82 (s, 2H, NH$_2$), 6.30 (s, 2H, NH$_2$), 7.91 (d, 4H, aromatic), 8.67 (d, 4H, aromatic); (Figure S5: ESI for ^{1}H NMR spectra)

***cis*-[Co{5-(4-bromophenyl)-tetrazolato}$_2$(en)$_2$]ClO$_4$ (*cis*-6) and *trans*-[Co{5-(4-bromophenyl)-tetrazolato}$_2$(en)$_2$]ClO$_4$ (*trans*-6) :**

Solid cobalt diazide complex *trans*-[Co(N$_3$)$_2$(en)$_2$]ClO$_4$ (0.12 g, 0. 33 mmol) **1a** and 0.54 (3 mmol) of 4-bromobenzonitrile in 5 mL of DMF was taken in a cylindrical pyrex tube and it was irradiated for 3 hrs at 130 °C. After removing the solvent *in vacuo* the resulting reddish-brown residue was washed several times with diethyl ether. The brown powder yielded was found to be a mixture of *cis*- and *trans*-compound in a tentatively ratio of 4:1 (Figure S6: ESI for ^{1}H NMR spectra). However the mixtures could not be separated by ion-exchange method as both the compound is getting decomposed in column. Recrystallization of the brown powder from methanol/diethyl ether mixtures provides crystalline compound which has been found to be mixture again. However, it was possible to grow the single crystals of *cis*-variety only by this method.

***cis*- and *trans*-[Co{5-(4-bromophenyl)-tetrazolato}$_2$(en)$_2$]ClO$_4$ (*cis*- and *trans*-6):** Yield: 54% IR (KBr, cm^{-1}): $\nu_{C=N}$ 1666. ClO$_4$ 1126. Anal. Calc. for $C_{18}H_{24}N_{12}O_4Br_2CoCl$ (726.65) :C 29.72; H 3.30; N 23.11; Found : C 30.00; H 3.62; N 22.98; MS(ESI): m/z = 627.18 [M]$^+$. ^{1}H NMR :δ_H (400 MHz, d$_6$DMSO, Me$_4$Si): 2.32-2.88 (m,8H,CH$_2$), 4.52, 4.91, 5.80, & 6.27 (all singlet, 8H, from cis variety) 5.41 (s, 8H, from trans variety) 7.66-8.10 (m, 8H, aromatic); (Figure S7: ESI for ^{1}H NMR spectra)

***cis*-[Co(5-phenyltetrazolato)$_2$(en)$_2$]ClO$_4$ (*cis*-7) and *trans*-[Co(5-phenyltetrazolato)$_2$(en)$_2$]ClO$_4$ (*trans*-7):** Solid cobalt diazide complex [Co(N$_3$)$_2$(en)$_2$]ClO$_4$ (0.12 g, 0. 33 mmol) **1a** and 2 mL of benzonitrile were added to a cylindrical pyrex tube and 3 mL of DMF was also added into it. The system was placed in the focused microwave reactor. The reaction mixture was left under irradiation for 1 h at 130 °C. The solvent was then removed *in vacuo* and the resulting residue was treated with diethyl ether to obtain a reddish-brown powder which was found to be a mixture of *cis*- and *trans*- variety tentatively in 9:1 ratio (Figure S8: ESI for ^{1}H NMR spectra). The mixture was separated by ion-exchange method as previously described for other compounds and then separately recrystallized from methanol/ether mixture. However, only the *cis*-variety produced some crystals suitable for X-ray analysis.

***cis*-[Co(5-phenyl-tetrazolato)$_2$(en)$_2$]ClO$_4$.MeOH (*cis*-7):** Yield: 28% IR (KBr, cm^{-1}): $\nu_{C=N}$ 1640. ClO$_4$ 1048. Anal. Calc. for $C_{19}H_{26}N_{12}ClCoO_5$ (596.9) : C 38; H 4.61; N 29.55; Found : C 37.56; H 4.92; N 28.72; MS(ESI): m/z = 469.16 [M]$^+$. ^{1}H NMR :δ_H (400 MHz, DMSO- d_6, Me$_4$Si): 2.27-2.89 (m,8H,CH$_2$), 4.63 (s, 2H, NH$_2$), 4.99 (s, 2H, NH$_2$), 5.79 (s, 2H, NH$_2$), 6.27 (s, 2H, NH$_2$), 7.42-7.98 (m, 10H, aromatic); (Figure S9: ESI for ^{1}H NMR spectra).

***trans*-[Co(5-phenyl-tetrazolato)$_2$(en)$_2$]ClO$_4$.MeOH.4C$_6$H$_5$CN (*trans*-7):** Yield : 6% IR (KBr, cm^{-1}): $\nu_{C\equiv N}$ 2230 $\nu_{C=N}$ 1637. ClO$_4$ 1046. Anal. Calc. For $C_{47}H_{46}N_{16}ClCoO_5$ (1009.35) : C 55.87; H 4.55; N 22.19; Found : C 55.56; H 4.25; N 22.02; MS(ESI): m/z = 469.16 [M]$^+$. ^{1}H NMR :δ_H (400 MHz, DMSO- d_6, Me$_4$Si): 2.01 (s, 4H, CH$_2$), 2.26 (s, 4H, CH$_2$), 4.47 (s, 8H, NH$_2$), 6.49-7.18 (m,10H + 20H,5-phenyltetrazole + benzonitrile); (Figure S10: ESI for ^{1}H NMR spectra).

X-ray crystallography. Single crystal X-ray structural studies of **(*cis*-2), (*cis*-3), (*trans*-4), 5** and **7** were performed on a CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer. Data for all the complexes were collected at 293(2) K except for (***cis*-3), 5** and **7** for which it was at 150(2) K using graphite-monochromated Mo Kα radiation (λ_α = 0.71073 Å). The strategy for the Data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard 'phi-omega scan techniques and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least-squares with SHELXL-97, refining on F^2 .[15]

The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally

$1.2U_{eq}$ of their parent atoms. The crystal and refinement data are summarized in Table 1, and selected bond distances and bond angles for ***cis*-2**, ***cis*-3**, ***trans*-4** and **(*cis*-5)-(*cis*-7)** are shown in Table 2a-Table 2f and Table S1(**ESI)** respectively **.**

However, the Single crystal X-ray diffraction data collections for the compound ***cis*-6** was performed using Bruker-APEX-II CCD diffractometer with graphite monochromated MoKα radiation (λ =0.71073 Å). The structures were solved by SIR-92[16] available in WinGX, which successfully located most of the non-hydrogen atoms. Subsequently, least square refinements were carried out on F^2 using SHELXL-97 (WinGX version)[15] to locate the remaining non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically and most of the hydrogen atoms were refined isotropically on calculated positions using a riding model.

Liberation of 5-substituted tetrazoles from Cobalt-complex :

Following method has been adopted for the release of the pure tetrazoles from the corresponding cobalt-tetrazolato complexes. In a typical example 0.1 g (0.164 mmol) of complex ***cis*-2** was taken in 10 mL of methanol and about 0.069 g (1.064 mmol) of NaN_3 dissolved in 10 mL of methanol was added into it. The reaction mixture was refluxed for 2 hrs. It gives no precipitate. The solution was filtered. The filtrate was evaporated to dryness under reduced pressure. The solid obtained was washed several times with diethyl ether and the washing was concentrated to obtain a colorless solid which was identified as 5-Phenyl-1*H*-tetrazole. Different tetrazoles were isolated in moderate to good yields (40 to 60%) and characterized by ESI mass spectroscopy furnishing similar data reported elsewhere.[17-25] All the tetrazoles were identified in their molecular protonated form $[MH]^+$ in ESI-MS spectra.

Results and Discussions

Synthesis and isolation of metal complexes and 5-substituted tetrazoles

Treatment of the diazidocobalt (III) complex *cis*-[$Co(N_3)_2(en)_2$]NO_3 **1** under microwave irradiation with the respective organonitriles RCN [R = 3-NC_5H_4 , 4-NC_5H_4 and 4-BrC_6H_4] gives the corresponding bis(tetrazolato) complexes [$Co(N_4CR)_2(en)_2$]NO_3 (Scheme 1). Use of microwave technique in metal assisted cycloaddition reaction is well known as it can drive the reaction much faster than the conventional refluxing method.[7,8] Reaction with 3-cyanopyridine furnished a mixture of *cis*- and *trans*- isomers of tetrazolato complex (***cis*-2** & ***trans*-2**) tentatively in 1:4 ratio (In absence of any other clear cut demarcation between both the isomers calculations are based on the integration of ^{1}H NMR peak observed due to nitrogen protons in ethylenediamine for *cis*- and *trans*- isomer respectively). However, reaction with 4-cyanopyridine yielded purely *cis*- isomer (***cis*-3**) as reddish-brown product. A similar reaction with 4-bromobenzonitrile furnished exclusively *trans*- isomer of bis(tetrazolato) complex (***trans*-4**) indicating a possible role of remote substitution at 5-position of phenyl ring for the preferential geometry of the cycloadded complex. In all the reactions DMF was used as the solvent because of poor solubility of the precursor complexes in other common organic solvents. In view of the above findings we were interested to check the outcome when the starting material is in *trans*-configuration. As there is no report to the best of our knowledge of existence of any compound like *trans*-[$Co(N_3)_2(en)_2$]NO_3, therefore we have synthesized a known compound *trans*-[$Co(N_3)_2(en)_2$]ClO_4 **1a** as per literature procedure.[14] Upon reaction of **1a** with 4-cyanopyridine, 4-bromobenzonitrile and benzonitrile we have obtained mixture of *cis*- and *trans*- isomers of bis(tetrazolate)complexes [$Co(N_4CR)_2(en)_2$]ClO_4 in tentatively 5:2, 4:1 and 9:1 ratio, respectively (Scheme 2). This result indicates a possible role of counter-anion to dictate the preferential isomer for the tetrazolate complexes. However only *cis*-isomer of tetrazolate complex synthesized from 4-cyanopyridine has been separated by ion-exchange chromatographic method (***cis*-5**). A similar effort to separate the isomers of bromo-substituted tetrazolato complexes (***cis*-6** and

trans*-6**) remained futile as both the compound decomposed in the ion-exchanged column. However, both the geometrical isomers (cis*-7** & ***trans*-7**) of [Co(5-phenyltetrazolato)$_2$(en)$_2$]ClO_4 can be separated by ion-exchange column chromatography.

All the reaction were carried out by focussed microwave radiation at 130 ° C for 1h-3hrs. Most of the complexes are soluble in methanol, dichloromethane and DMF.

All the complexes (except ***trans*-5 and *cis*-6 & *trans*-6)** have been characterized by elemental analyses, IR, ESI-MS and ^{1}H NMR spectroscopy. As ***cis*-6** and ***trans*-6** could not be separated from the mixture therefore it was characterized as a whole by IR, elemental analysis, ESI-MS and ^{1}H NMR spectroscopy . The IR spectra of all the compounds do not show the typical azide band at *ca.* 2078 and 2019 cm^{-1} for complex **1** and 2016 cm^{-1} for complex **1a** and display a new strong band within the 1612–1665 cm^{-1} range due to the tetrazole ring, in agreement with the literature.[7-8,26-27] In ESI-MS in all bis(tetrazolate) complexes the molecular ion peaks have been observed confirming the presence of bistetrazolate ligand in the metal complex.

The ^{1}H NMR spectroscopy was used to determine the relevant ratio of the geometrical isomers that have been obtained as a result of cycloaddition reactions. In absence of any other clear cut distinguishable protons between *cis*- and *trans*- isomers, integration of NH_2 protons have been used to calculate a tentative ratio of geometrical isomers generated in the solution state. Each individual isomers have been further characterized with the help of the ^{1}H NMR spectroscopy. All the *cis*- isomers show four signals within the range 4.51-6.37 ppm typical for nitrogen protons of ethylenediamine characteristic of *cis*-[Co(en)$_2$] group,[28] while CH_2 groups of ethylenediamine show a more complex multiplet within the range 1.91 - 2.90 as reported elsewhere.[29] The results obtained are in good agreement with similar types of (ethylenediamine)cobalt complexes reported earlier.[30-32] All the *trans*- isomers show a single peak in the range of 4.47-5.41 ppm attributed to nitrogen protons of ethylenediamine while the CH_2 protons are observed in the range of 2.01-2.45 ppm. Some additional protons in the aromatic region observed for compound ***trans*-7** may be attributed to the presence of free benzonitrile which might have been entrapped during the crystallization of the compound. This fact is also further supported by the presence of a small nitrile peak at 2130 cm^{-1} in the IR spectrum of the compound and elemental analysis result.

Liberation of 5-substituted tetrazole from bis(tetrazolato) complexes were carried out by treating precursor tetrazolato-metal complexes with excess of sodium azide in methanol. After refluxing the mixture for 2 hours the filtrate was evaporated to dryness and the residue was washed with diethyl ether which upon concentration provides respective 5-substituted tetrazoles in its neutral form rather than the sodium salt as it is evident by the presence of protonated form of molecular ion peak $[MH]^+$ in ESI-MS spectroscopy. In all probability the tetrazolate ion picks up one proton from the water present in the solvent. Apart from ESI-MS, all these tetrazoles have been identified using ^1H and ^{13}C NMR which corresponds well with the earlier reports.[17-25]

The Co^{+3} ion with d^6 configuration in an octahedral crystal field, in the solution state shows the presence of mostly one absorption band due to the d–d transitions in the octahedral CoN_6 crystal field. The strong bands which is observed in the range of 443.7 nm-450.9 nm is assigned to the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition while the absorptions due to the transition $^1A_{1g} \rightarrow {}^1T_{2g}$ are mostly masked (correlated as very weak shoulder) due to the presence of long tail of the charge-transfer peaks.[33,34] The presence of other electronic transitions which appear in the UV region can be correlated to the $\pi \rightarrow \pi^*$ transition in the ligand. (Table 3). One thing is to be noted here is that though there are not much differences have been observed in the absorption spectra of different isomers however it should be mentioned here that they are not totally identical as well (**Figure S11 : ESI**).

Crystal structures of *cis*-[Co{5-(3-pyridyl)-tetrazolato}$_2$(en)$_2$]NO_3.DMF (*cis*-2), *cis*-[Co{5-(4-pyridyl)-tetrazolato}$_2$(en)$_2$]NO_3.Et_2O (*cis*-3), *cis*-[Co{5-(4-pyridyl)-tetrazolato}$_2$(en)$_2$]ClO_4.H_2O (*cis*-5), *cis*-[Co{5-(4-bromophenyl)-tetrazolato}$_2$(en)$_2$]ClO_4 (*cis*-6) and *cis*-[Co(5-phenyl-tetrazolato)$_2$(en)$_2$].ClO_4 (*cis*-7)

The nature of all the above complexes have been established by single-crystal X-ray crystallography. The corresponding crystallographic data are given in Table 1 and selected bond distances and angles in Table 2a-2f. The corresponding hydrogen bonding interactions are summarized in Table S1(ESI). X-ray structure determination of ***cis*-2** compound revealed that there are two crystallographically independent complex molecules exist with very similar geometries in the unit cell (fig **3**). The central ion is situated in a distorted octahedral environment. Both the tetrazolate anions coordinate in a monodentate fashion and their disposition around the metal center is *cis*. The dihedral angle between the coordinated tetrazoles and substituted pyridyl rings are found to be 7.96 ° and 10.44 °, respectively for first cobalt center. However, for the second cobalt center they are 3.40 ° and 3.73 °, respectively. The complex cation and non-coordinated anion are associated in ionic pairs through very close hydrogen bonding interaction from both the ethylenediamine molecules towards the oxygen atoms of nitrate ion.

The first type of molecules are coordinated to different surrounding nitrate ions through N2-H2B ··O555, N4-H4B ··O555, C1-H1C ··O111, N1-H1B ··O111, N1-H1B ··O222 and C16-H16 ··O222 (fig **S12a**). The second independent molecule is also connected to the counter-ions by several similar hydrogen bonding connections. Further these molecules are interconnected through pyridyl nitrogen [N3-H3B ··N23 and N4-H4A ··N28] to form two strands of one-dimensional chain structure interconnected through hydrogen bonding *via* nitrate anions along *a*-axis (fig **S12b**). (N2-H2B ··O555, N4-H4B ··O555, N1-H1B ··O111, C1-H1C ··O111, N16-H16 ··O011, N17-H17A ··O011, N15-H15B ··O666, N17-

H17B ···O666). One of the independent molecule is furthermore stabilized by hydrogen bond formation between DMF and one of the en molecule attached to the metal centre (N1-H1A-O888). There are two types of nitrate ions. One is forming a hydrogen bonded 1D polymer by forming bridges between the two crystallographically independent molecule the other is helping to join the two strands together by hydrogen bond formation (fig **S12c**).

Compound ***cis*-3** which crystallizes in monoclinic space group P2_1/c, shows crystallographically one independent structure. The *cis* configuration of the compound has been enforced by weak H-bonded interaction between one nitrate ion and two en molecules attached to the same metal center (N1-H1A ···O111, N4-H4B ···O111, N1-H1A ···O333) (fig **4**). Two such molecules are hydrogen bonded with each other via mutual interaction through N4-H4A ···N14 involving pyridyl nitrogen atom and one of the hydrogen of en ligand (fig **S13a**). These dimers are further mutually interconnected via C16-H16 ···N9 forming a ladder type of structure along c-axis (fig **S13b**). These strand type ladder structures are interconnected by hydrogen bonded nitrate structure N3-H3B ···O222, N2-H2B ···O222, N4-H4B ···O111 in a three dimensional way to form hydrogen bonded framework (fig **S13c**). Diethylether molecule has been also observed as the solvent of crystallization which is also associated with one of the ethylene diamine hydrogen via hydrogen bonding (N1-H1B ···O101).

The single crystal X-ray structure of ***cis*-5** confirms the formation of *cis* configuration of the compound. It crystallizes in monoclinic space group P 21/c and exhibit 3-D supramolecular arrays formed by hydrogen bond interactions. In **5**, the Co(III) resides in an octahedral co-ordination geometry (fig **5**). Each cationic unit is connected to three neighbouring oxygen atoms of the perchlorate anion via N1-H1B ···O333, N1-H1B ···O444, C2-H2A ···O333, N4-H4A ···O333, N2-H2A ···O111, C3-H3A ···O111 and N3-H3A ···O444 interactions.(fig **S14a**). Furthermore in this network, each unit is connected to two adjacent units through the pyridyl nitrogen atom and hydrogens of en ligand via N3-H3B ···N14, C2-H2B ···N13 and N2-H2B ···N13 interactions along *b*-axis.(fig **S14b**). All of these H-bonds altogether form a 3D supramolecular framework structure.

Though the refinement factor for the crystal structure of compound ***cis*-6** is on higher side however it unequivocally indicates the two tetrazolate ions coordinate the metal ion in cis-fashion through N^2-atoms (fig **6**). The dihedral angle between tetrazole and phenyl ring is found to be 22.73 ° for both the ligands. Each perchlorate ions is found to be connected with three molecules through three equivalent oxygen atom C1-H1A ···O1 and C9-H9 ···O1. This is further supported by N1-H1B ···O2 hydrogen bonding (fig **S15a**) and may be also helping to enforce the *cis*-geometry within the molecule. The independent molecules are packed along *a*-axis and *b*-axis through H-bonding between different molecules and the perchlorate counter ions helps in forming a hydrogen bonded 2D polymer in *ab*-plane. All these network which are running in the direction of *ab*-plane orients in such a way that being with cis conformation the *para*-substituted bromine atoms get stacked one upon another along *b*-axis as well as *a*-axis (fig **S15b**). However long distance Br ···Br interactions between the bromine atom of one molecule and two other bromine atoms of neighbouring molecules [Br-Br 4.969 Å] may also contribute for the preferential *cis*- geometry of complex ***cis*-6**.

Compound ***cis*-7** crystallizes in space group $P2_12_12_1$ and the metal nitrogen distances are found to be in the range of 1.906-1.972 Å, typical for the Co^{3+} ion. The tetrazolato ligands are *cis* to each other (fig **7**). The counter perchlorate ions are found to be connecting different molecules via hydrogen bonding *viz*. N1-H1A ···O222, C3-H3D ···O222, N3-H3B ···O333, N3-H3B ···O555, N4-H4B ···O555, C3-H3C ···O444, N4-H4B ···O444 and N2-H2B ···O444 (fig **S16a**) leading to the formation of a hydrogen bonded 3D network (fig **S16b**).

Crystal structure of *trans*-[Co{5-(4-bromophenyl)-tetrazolato}$_2$(en)$_2$]NO_3 (*trans*-4) :

Compound ***trans*-4** have crystallized in space group P-1 having two crystallographically independent complex molecules with very similar geometries (fig **8**). Two tetrazolato ligands here coordinate in *trans* fashion and the twist of phenyl ring with respect to coordinated tetrazole rings are different for two independent molecule. The dihedral angle has been found to be 4.74 ° for the first type where as for the second type this is about 25.02 ° for both the 5-substituted tetrazole ligands. The twist in the ring can be attributed because of the H-bond formation between ethylenic hydrogen of one molecule and tetrazolyl nitrogen of the adjacent complex (N5-H5B ··· N11) (fig **S17a**). These molecules are further interconnected with different ethylenic hydrogen and tetrazolyl nitrogen (N5-H5B ··· N11, N8-H8A ··· N1) to form a 1D-chain along b-axis (fig **S17b**). This chain is further supported by nitrate ions which connects four different molecules surrounding it by hydrogen bonds (C7-H7 ··· O111, N8-H8B ··· O111, N8-H8B ··· O333, N6-H6B ··· O333, C9-H9A ··· O222) which altogether forms a 2D-network in *ab*-plane (fig **S17c**). Furthermore one DMF molecules has been found hydrogen bonded to the first type of cobalt center *via* N5-H5A ··· O101 hydrogen bond. The consequence is that all 5-substituting bromine atoms are found to be aligning in a single line when viewed along a- or b-axis (fig **S17d**). The nearest Br ··· Br [Br(1) ··· Br(2)] contact has been found to be 4.082 Å slightly larger than the sum of the van der Waals radii sum. However, the formation of long distance Br ··· Br interaction could be one of the driving force for the crystallization of the molecule in *trans*- geometry.

Computational Studies:

Density functional calculations (DFT) are carried out to understand the driving force behind the crystallization of complex ***trans*-4** in the preferred geometry. Interestingly, reaction of 4-bromobenzonitrile with *trans*-[Co$(N_3)_2$$(en)_2$]$ClO_4$ produced predominantly *cis*- isomer (***cis*-6)**. These two complexes (***trans*-4 and *cis*-6)** are considered for our calculation as both the complexes having same set of ligands (R = 4-BrC6H4) though different counter anions.

Therefore to understand the factors which may be playing a role in preferred geometry we have modelled these two complexes (***trans*-4** and ***cis*-6**) for our comparative study.

We have studied these complexes in their solid state structures retaining their space group geometry. Periodic boundary conditions are used for the three dimensional structure modelling. The first-principles calculations are used using projected augmented wave (PAW) method as implemented in the Vienna ab-initio simulation package (VASP) for their structural relaxation.[35-37] The exchange-correlation interaction is treated in the level of the GGA using Perdew-Burke-Ernzerhof (GGA-PBE).[38] We have calculated the van der Waals corrected interaction energies using the semi-empirical correction of Grimme[39] as available with VASP for the accurate treatment of the weak intermolecular interactions between the metal complexes. Our calculations show both the complexes (***trans*-4** and ***cis*-6**) are minima in their potential energy surfaces. The calculated van der Waals interaction energies for the complexes ***trans*-4** and ***cis*-6** are 4.90 and 4.30 eV (per molecular unit) respectively. Therefore, the van der Waals interaction energy is more for the *trans geometry*. Interestingly, in the *trans* (***trans*-4**) geometry, we found one solvent molecule (DMF) is trapped for each molecular units. To understand the possible role of solvent for preferred geometry, we have removed the solvent from the crystal structure of ***trans*-4** complex and relaxed the structure retaining in the same space group geometry. We find the calculated van der Waals interaction energies reduced from 4.90 eV to 3.99 eV per molecular unit. Therefore each solvent molecule is contributing around 20.98 kcal (0.91 eV) towards the total van der Waals interaction energies. Therefore the weak interaction directed by the solvent molecule possibly playing a major role in crystallizing the complex ***trans*-4** in *trans* geometry.

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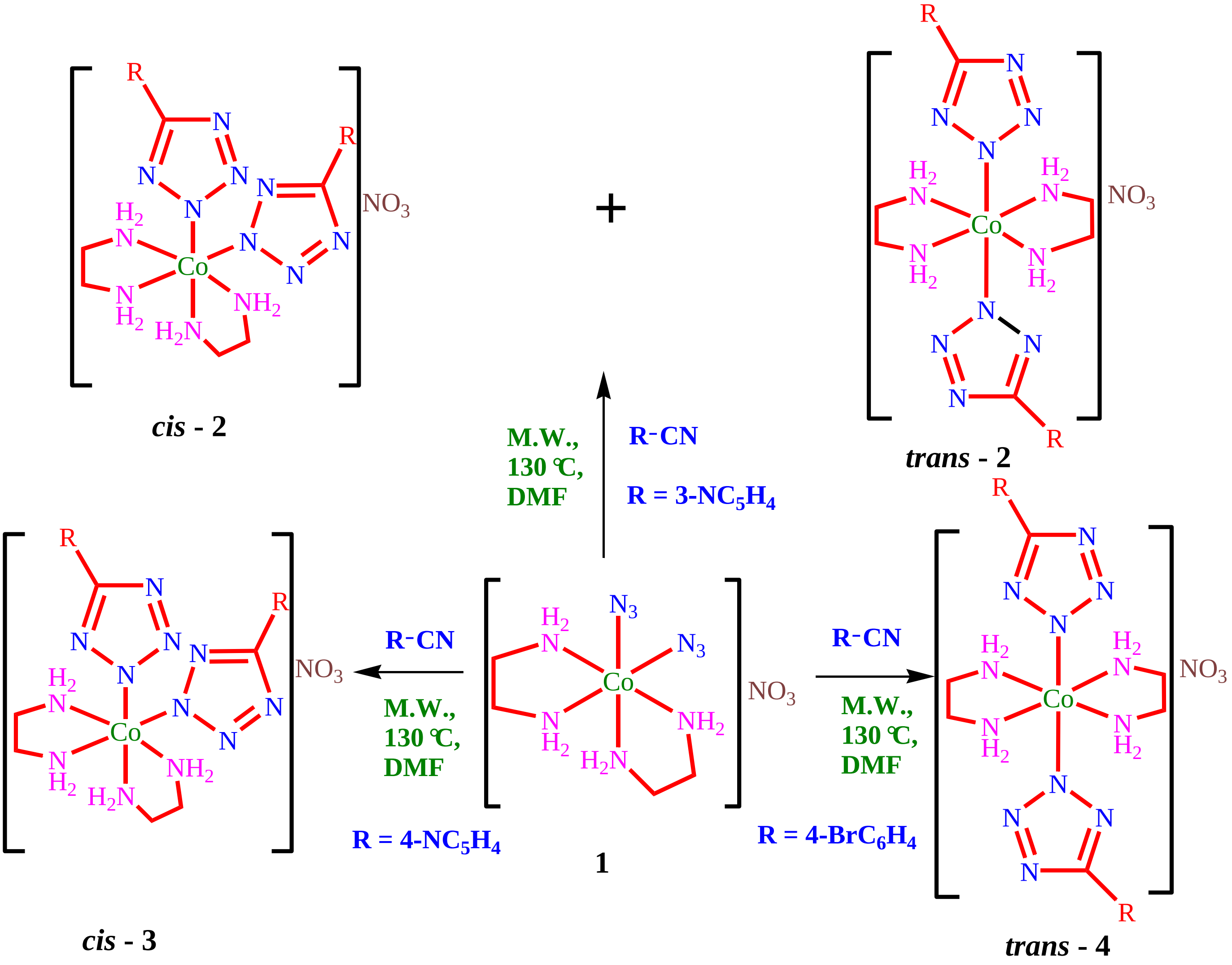
Appendix A. Supplimentary Materials

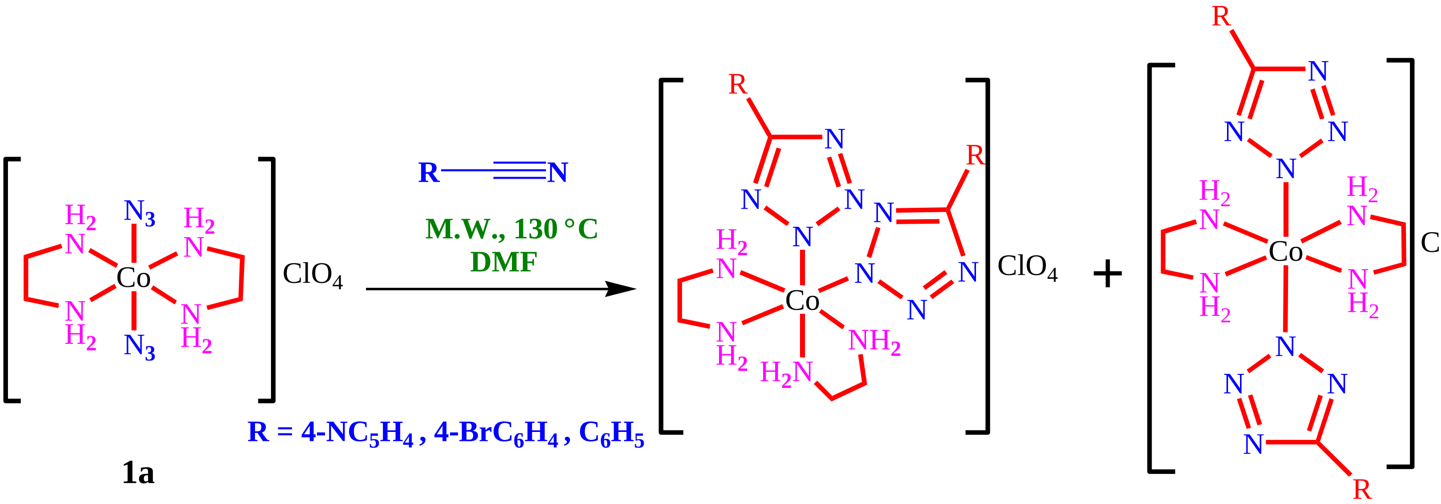
CCDC 933043-933047 and 935043 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Conclusions

In this work we have investigated the interaction of diazido complex *cis*-$[Co(N_3)_2(en)_2](NO_3)$ **1** and *trans*-$[Co(N_3)_2(en)_2](ClO_4)$ **1a** with various organonitriles under focussed microwave irradiation. Interaction of **1** with 3-cyanopyridine forms *cis*- and *trans*- isomers of cycloadded bis-tetrazolato complexes tentatively in 1:4 ratio. However interaction with 4-cyanopyridine produced exclusive *cis*-isomer of bis(tetrazolate) complex and reaction with 4-bromobenzonitrile produced bis(tetrazolate) complex in *trans* disposition indicating the role of remote substitution in phenyl ring in formation of the preferential isomer. The interaction of *trans*-$[Co(N_3)_2(en)_2]ClO_4$ under similar condition with 4-cyanopyridine, 4-bromobenzonitrile and benzonitrile furnished mixture of *cis*- and *trans*- isomers of bis(tetrazolate) complexes where the *cis*-geometry predominates. It has been assumed possibly the counter-anion which is helping the compound to crystallize and also interacting with the complex in solution state is also contributing to preferential geometrical isomer formation upon cycloaddition. Further, a DFT calculation study indicates that the trans isomer ***trans*-4** is getting more stabilized by means of van der Waals interaction through an extra DMF molecule (compared to ***cis*-6**)which is present as solvent of crystallization along with some Br...Br halogen interaction. Furthermore 5-substituted tetrazole can be isolated from the bis(tetrazolate) complex by treating it with excess sodium azide.


cis - 2
+
trans - 2
M.W., 130 ℃, DMF
R-CN
R = 3-NC$_5$H$_4$
cis - 3
R-CN
M.W., 130 ℃, DMF
R = 4-NC$_5$H$_4$
1
R-CN
M.W., 130 ℃, DMF
R = 4-BrC$_6$H$_4$
trans - 4
Co
N$_3$
NO$_3$
R

Scheme - 1



5 : R = 4-NC_5H_4 (*cis* - 5) + (trans - 5)

6 : R = 4-BrC_6H_4 (*cis* - 6) + (trans - 6)

7 : R = C_6H_5 (*cis* - 7) + (trans - 7)

Scheme - 2

Table 1 . Crystal Data and Structure Refinement of Complexes ***cis*-2, *cis*-3, trans-4**, ***cis*-5**, ***cis*-6** and ***cis*-7**

	***cis*-2**	***cis*-3**	***trans*-4**
Empirical formula	$C_{38}H_{48}N_{32}O_8Co_2$	$C_{20}H_{24}N_{15}O_4Co$	$C_{21}H_{31}N_{14}O_4CoBr_2$
Formula weight	1198.94	597.47	762.35
Wavelength(A)	0.71073	0.71073	0.71073
Temperature(K)	293(2)	150(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Colour and shape	Yellow needle	Yellow needle	Yellow needle
Space group	P 21 /c	P 21 /c	P-1
a/Å	18.5537(5)	11.6957(6)	8.5104(7)
b/Å	20.4481(7)	18.9480(6)	12.417(2)
c/Å	14.4208(5)	12.5618(3)	16.104(2)
α/degree	90	90	109.442(14)
β/degree	91.001(3)	92.388(4)	100.647(9)
γ/degree	90	90	95.584(10)
Volume($Å^3$)	5470.2(3)	2781.40(18)	1553.7(4)
Z	4	4	2
D_{calcd} /mg m^{-3}	1.456	1.427	1.672
μ(Mo Kα)/mm^{-1}	0.685	0.673	3.193
F(000)	2472	1232	788
Crystal size/mm	0.32 x 0.28 x 0.24	0.33 x 0.26 x 0.21	0.38 x 0.34 x 0.29
θ range(°)	3.00 to 25.00	3.17 to 25.00	3.05 to 25.00
Limiting indices	-22<=h<=22 -24<=k<=24 -17<=l<=17	-13<=h<=11 -22<=k<=22 -14<=l<=14	-10<=h<=10 -14<=k<=12 -19<=l<=19
Total/ unique no. of reflns.	31738 / 9616	15822 / 4888	10996 / 5454
R_{int}	0.0629	0.0387	0.0545
Data/restr./params.	9616 / 0 / 721	4888 / 25 / 361	5454 / 0 / 384
GOF(F^2)	1.026	1.034	1.057
R1, wR2	0.0589, 0.1390	0.0502 , 0.1328	0.0751, 0.2081
R1, wR2 (all data)	0.1020, 0.1721	0.0676, 0.1467	0.1078, 0.2381
Peak and hole (e $Å^{-3n}$)	0.729 and -0.449	0.587 and -0.316	0.907 and -0.719

	***cis*-5**	***cis*-6**	***cis*-7**
Empirical formula	$C_{32}H_{50}N_{28}O_9Co_2Cl_2$	$C_{18}H_{24}N_{12}O_4Br_2CoCl$	$C_{19}H_{26}N_{12}O_5CoCl$
Formula weight	1159.76	726.65	596.9
Wavelength(A)	0.71073	0.71073	0.71073
Temperature(K)	150(2)	293(2)	150(2)
Crystal system	Monoclinic	Trigonal	Orthorhombic
Color and shape	Yellow needle	Yellow needle	Yellow needle
Space group	P 21/c	P-3c1	P 21 21 21
a/Å	11.6499(7)	12.545(3)	13.0541(4)
b/Å	16.1363(13)	12.545(3)	13.3594(7)
c/Å	13.5916(11)	32.893(16)	14.8320(4)
α/degree	90.00	90.00	90
β/degree	95.163(6)	90.00	90
γ/degree	90.00	120.00	90
Volume(Å^3)	2544.7(3)	4483(3)	2586.63(17)
Z	4	6	10
D_{calcd} /mg m^{-3}	1.511	1.585	1.533
μ(Mo Kα)/mm^{-1}	0.834	3.381	0.823
F(000)	1192	2108	1232
Crystal size/mm	0.26 x 0.21 x 0.18	0.33 x 0.25 x 0.08	0.23 x 0.18 x 0.13
θ range(°)	2.94 to 25.00	1.24 to 20.92	3.14 to 24.99
Limiting indices	-13<=h<=13 -19<=k<=19 -16<=l<=14	-12<=h<=12 -12<=k<=12 -33<=l<=32	-15<=h<=15 -12<=k<=15 -17<=l<=17
Total/ unique no. of reflns.	21371 / 4471	33225 / 1589	18243 / 4554
R_{int}	0.0740	0.1818	0.0367
Data/restr./params.	4471 / 0 / 334	1589 / 0 / 164	4554 / 0 / 343
GOF(F^2)	1.067	1.156	1.104
R1, wR2	0.0678, 0.1706	0.0896, 0.2471	0.0418, 0.1103
R1, wR2 (all data)	0.0908, 0.1951	0.1374, 0.3084	0.0451, 0.1131
Peak and hole (e Å^{-3n})	0.820 and -0.715	1.762 and -0.819	0.524 and -0.474

Table 2a

Selected bond lengths (Å) and bond angles (°) for ***cis*-2**

Co(1)-N(5)	1.904(4)	N(5)-Co(1)-N(10)	91.90(16)
Co(1)-N(10)	1.907(4)	N(1)-Co(1)-N(4)	178.46(16)
Co(1)-N(1)	1.955(4)	N(5)-Co(1)-N(3)	174.28(16)
Co(1)-N(3)	1.958(4)	N(5)-Co(1)-N(2)	87.56(15)
Co(1)-N(2)	1.958(3)	N(10)-Co(1)-N(1)	90.31(16)
Co(1)-N(4)	1.952(4)		
N(5)-N(7)	1.305(5)		
N(7)-N(8)	1.341(5)		

Table 2b

Selected bond lengths (Å) and bond angles (°) for ***cis*-3**

Co(01)-N(10)	1.919(2)	N(10)-Co(01)-N(5)	87.98(12)
Co(01)-N(5)	1.919(3)	N(10)-Co(01)-N(2)	174.76(13)
Co(01)-N(4)	1.953(3)	N(10)-Co(01)-N(4)	91.38(11)
Co(01)-N(3)	1.953(3)	N(3)-Co(01)-N(1)	176.90(11)
Co(01)-N(1)	1.956(3)	N(4)-Co(01)-N(1)	92.42(12)
Co(01)-N(2)	1.956(3)		
N(5)-N(6)	1.314(4)		
N(6)-N(7)	1.340(4)		

Table 2c

Selected bond lengths (Å) and bond angles (°) for ***trans*-4**

Co(1)-N(3)	1.915(6)	N(3)#1-Co(1)-N(3)	180.0(3)
Co(1)-N(5)	1.956(5)	N(3)-Co(1)-N(6)	89.5(2)
Co(1)-N(6)	1.951(5)	N(6)-Co(1)-N(6)#1	180.0(3)
N(3)-N(2)	1.297(7)		
N(2)-N(1)	1.350(8)		

Table 2d

Selected bond lengths (Å) and bond angles (°) for ***cis*-5**

Co(1)-N(9)	1.902(4)	N(9)-Co(1)-N(5)	92.38(17)
Co(1)-N(4)	1.960(4)	N(9)-Co(1)-N(3)	90.79(17)
Co(1)-N(5)	1.913(4)	N(5)-Co(1)-N(3)	89.99(17)
Co(1)-N(3)	1.942(4)	N(9)-Co(1)-N(1)	90.19(17)
Co(1)-N(1)	1.949(4)	N(5)-Co(1)-N(1)	90.12(18)
Co(1)-N(2)	1.955(4)	N(3)-Co(1)-N(1)	179.01(17)
N(5)-N(6)	1.311(6)	N(9)-Co(1)-N(2)	175.50(17)
N(5)-N(8)	1.341(6)	N(5)-Co(1)-N(2)	89.40(17)
N(6)-N(7)	1.345(6)	N(3)-Co(1)-N(2)	93.34(17)
N(9)-N(10)	1.321(6)	N(1)-Co(1)-N(2)	85.67(17)
N(9)-N(12)	1.339(5)	N(9)-Co(1)-N(4)	86.82(18)
N(10)-N(11)	1.344(6)	N(5)-Co(1)-N(4)	175.79(18)
		N(3)-Co(1)-N(4)	85.89(18)
		N(1)-Co(1)-N(4)	94.02(19)
		N(2)-Co(1)-N(4)	91.70(18)

Table 2e

Selected bond lengths (Å) and bond angles (°) for ***cis*-6.**

Co(1)-N(4)	1.936(11)	N(4)-Co(1)-N(4)#3	90.9(6)
Co(1)-N(4)#3	1.936(11)	N(4)-Co(1)-N(1)	91.6(4)
Co(1)-N(1)	1.935(9)	N(4)#3-Co(1)-N(1)	91.1(4)
Co(1)-N(1)#3	1.935(9)	N(4)-Co(1)-N(1)#3	91.1(4)
Co(1)-N(2)#3	1.943(10)	N(4)#3-Co(1)-N(1)#3	91.6(4)
Co(1)-N(2)	1.943(10)	N(1)-Co(1)-N(1)#3	176.1(6)
N(4)-N(5)	1.312(13)	N(4)-Co(1)-N(2)#3	175.7(4)
N(4)-N(3)	1.328(13)	N(4)#3-Co(1)-N(2)#3	89.2(4)
N(6)-N(5)	1.321(14)	N(1)-Co(1)-N(2)#3	92.8(4)
		N(1)#3-Co(1)-N(2)#3	84.5(4)
		N(4)-Co(1)-N(2)	89.2(4)
		N(4)#3-Co(1)-N(2)	175.7(4)
		N(1)-Co(1)-N(2)	84.5(4)
		N(1)#3-Co(1)-N(2)	92.8(4)
		N(2)#3-Co(1)-N(2)	91.1(6)

Symmetry transformations used to generate equivalent atoms:

#1 -x+y+2,-x+1,z #2 -y+1,x-y-1,z

#3 y+1,x-1,-z+1/2 #4 -x+y+1,-x+1,z

#5 -y+1,x-y,z

Table 2f

Selected bond lengths (Å) and bond angles (°) for ***cis*-7**

Co(01)-N(1)	1.935(4)	N(1)-Co(01)-N(2)	86.0(1)
Co(01)-N(2)	1.972(3)	N(1)-Co(01)-N(3)	91.5(1)
Co(01)-N(3)	1.947(3)	N(1)-Co(01)-N(4)	177.5(1)
Co(01)-N(4)	1.962(4)	N(1)-Co(01)-N(5)	90.8(1)
Co(01)-N(5)	1.920(3)	N(1)-Co(01)-N(9)	92.1(1)
Co(01)-N(9)	1.906(3)	N(2)-Co(01)-N(3)	92.7(1)
N(5)-N(6)	1.343(4)	N(2)-Co(01)-N(4)	94.0(1)
N(5)-N(7)	1.310(6)	N(2)-Co(01)-N(5)	175.7(1)
N(7)-N(8)	1.339(5)	N(2)-Co(01)-N(9)	86.9(1)
N(9)-N(10)	1.327(5)	N(3)-Co(01)-N(4)	85.9(1)
N(9)-N(12)	1.345(4)	N(3)-Co(01)-N(5)	90.2(1)
N(10)-N(11)	1.345(4)	N(3)-Co(01)-N(9)	176.3(1)
		N(4)-Co(01)-N(5)	89.4(1)
		N(4)-Co(01)-N(9)	90.4(1)
		N(5)-Co(01)-N(9)	90.4(1)

Table 3 . Absorption Spectra of compounds ***cis*-2,trans-2, *cis*-3, *trans*-4, *cis*-5, *cis*-6 and *cis*-7** in Methanol.

Compound no.	**λ nm , (ε, $M^{-1}cm^{-1}$)**
***cis*-2**	446.8 (180)
***trans*-2**	447.5 (171)
***cis*-3**	445.1 (147), 249.8 (22400), 202.5 (42200)
***trans*-4**	443.7 (174), 252.9 (47000), 203.5 (71300)
***cis*-5**	446.7 (165)
***trans*-5**	Cannot be separated
Mixture of *cis*-6 and *trans*-6	447.6 (72), 242 (137000), 204.6 (120900)
***cis*-7**	450.86 (72)
***trans*-7**	446.27 (91)

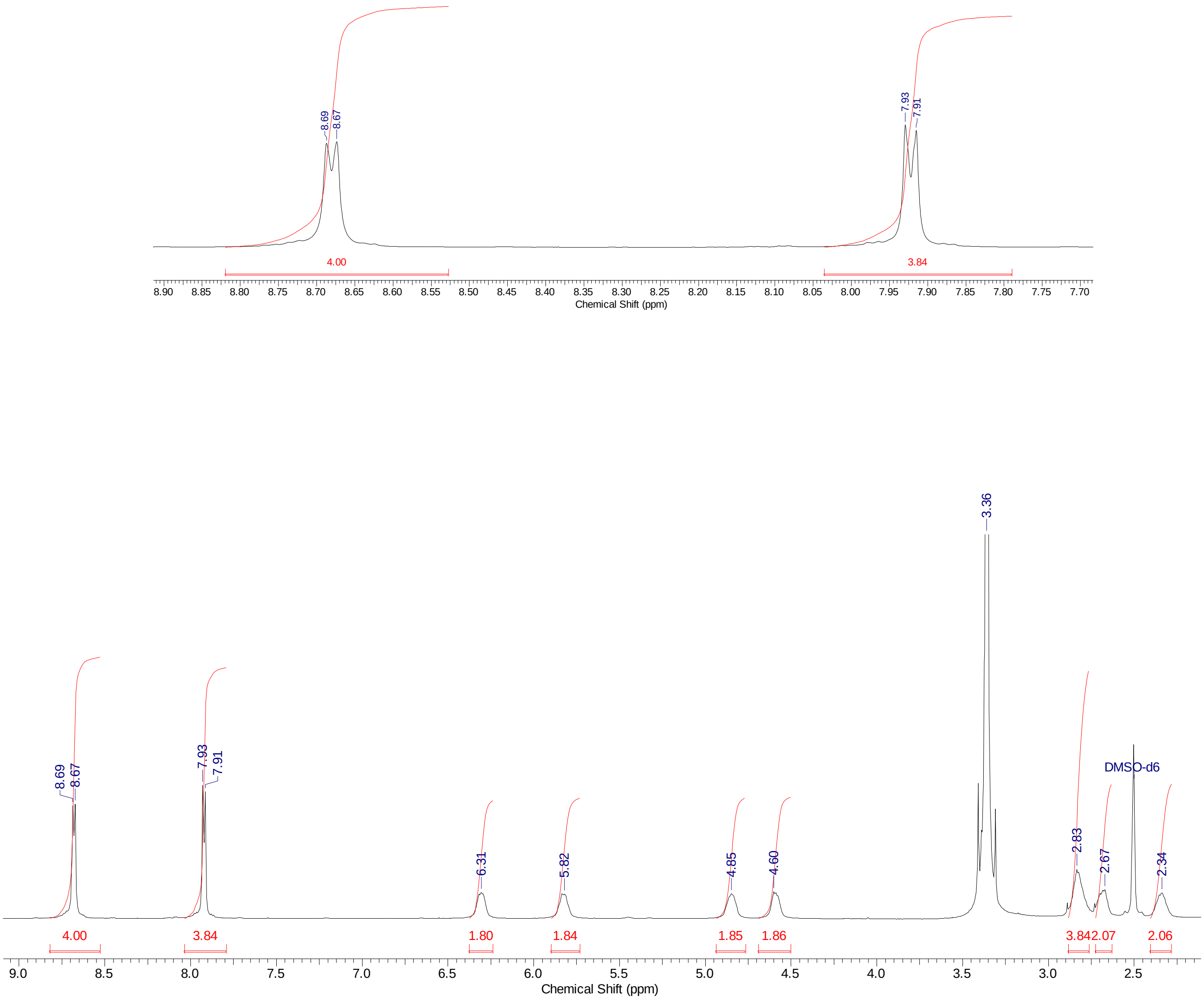
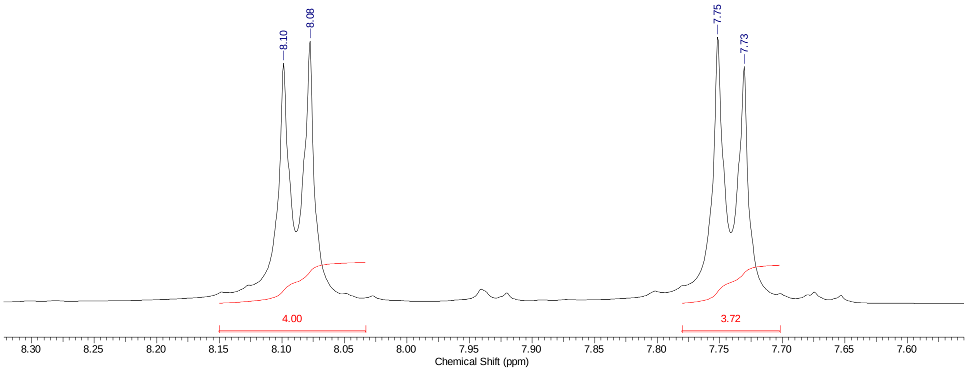


Figure 1. 1H NMR Spectra of *Cis*-3.



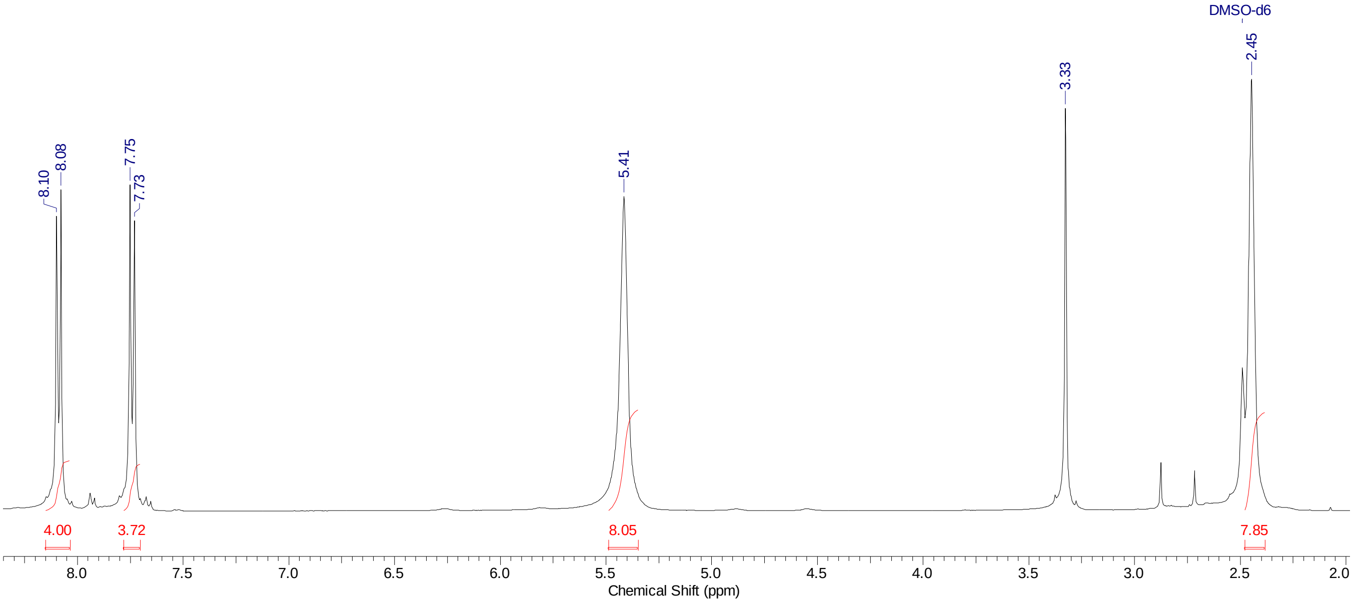


Figure 2. 1H NMR Spectra of *Trans*-4.

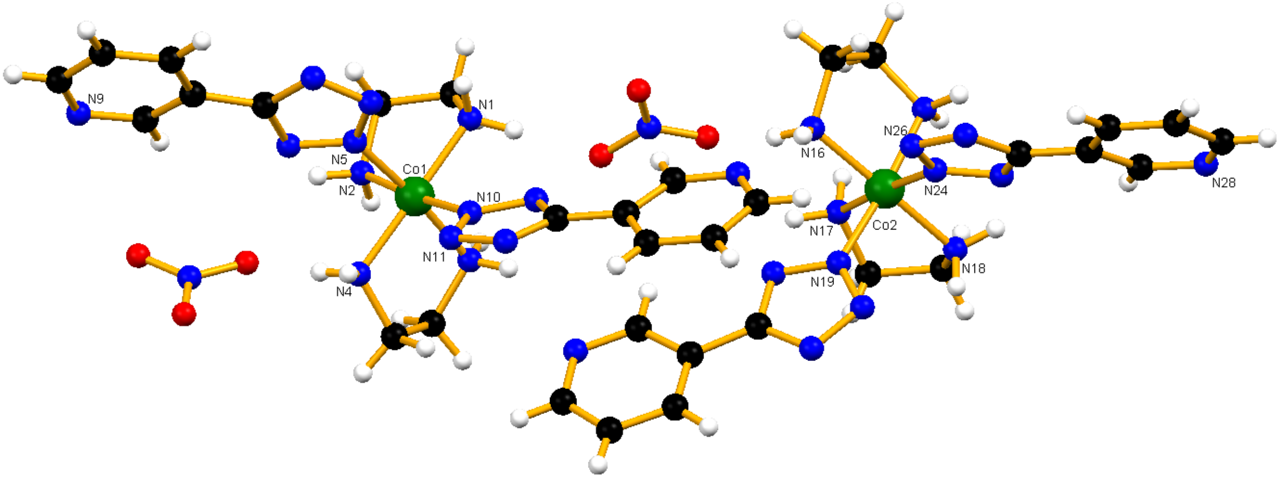


Fig. 3 View of two crystallographically independent complex molecules of compound ***cis*-2**.

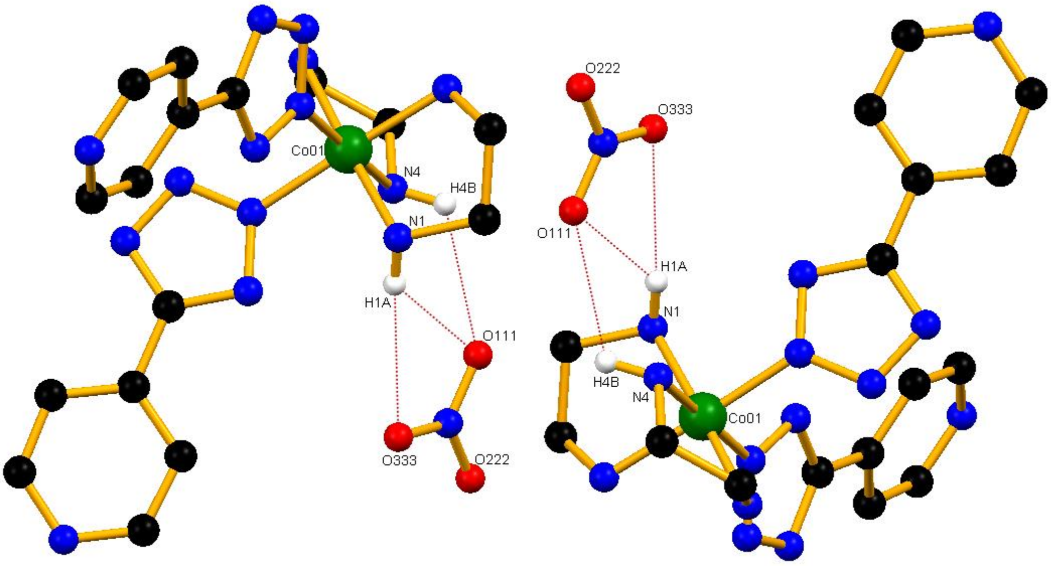


Fig. 4 View of weak H-bonded interaction between nitrate ion and two ethylenediamine molecules attached to the same metal center in ***cis*-3**.

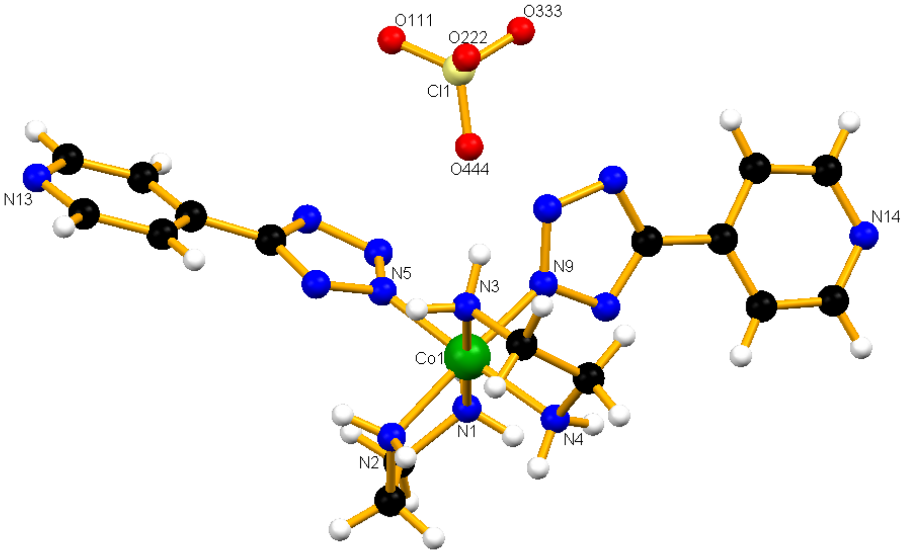


Fig. 5 View of local co-ordination geometry at the Co(III) centre in ***cis*-5** where tetrazolato ligands are *cis* to each other.

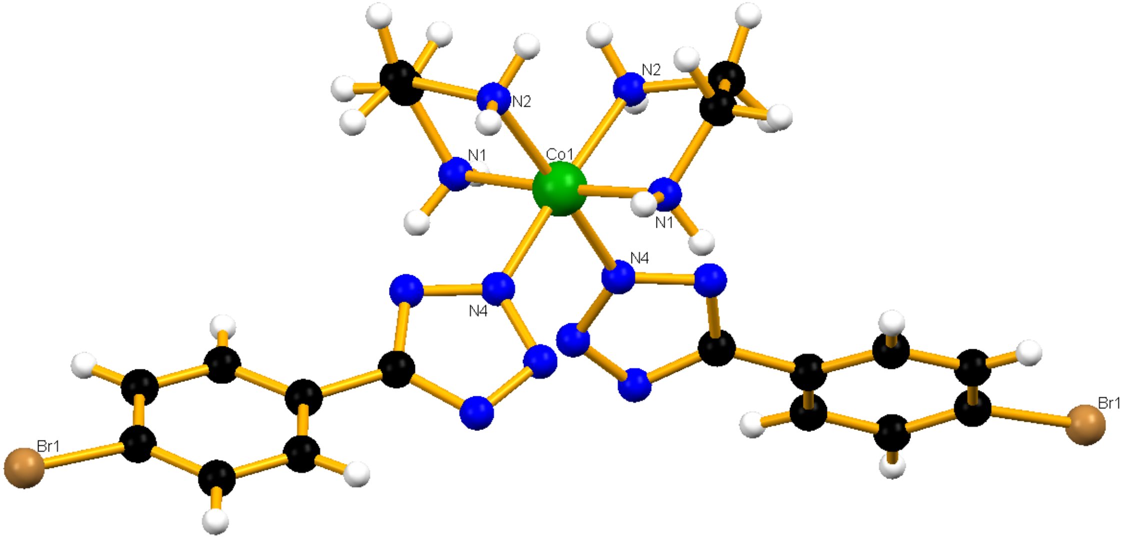


Fig . 6 Molecular structure of compound ***cis*-6.**

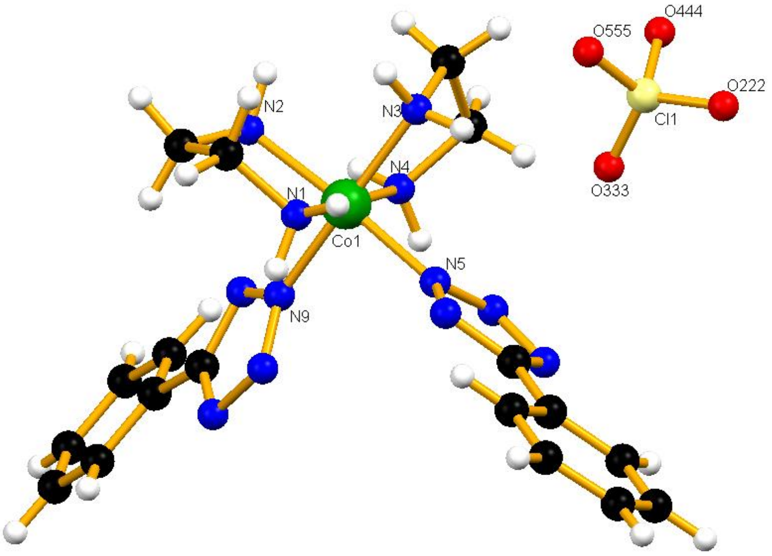


Fig. 7 View of local co-ordination geometry at the Co(III) centre in ***cis*-7**.

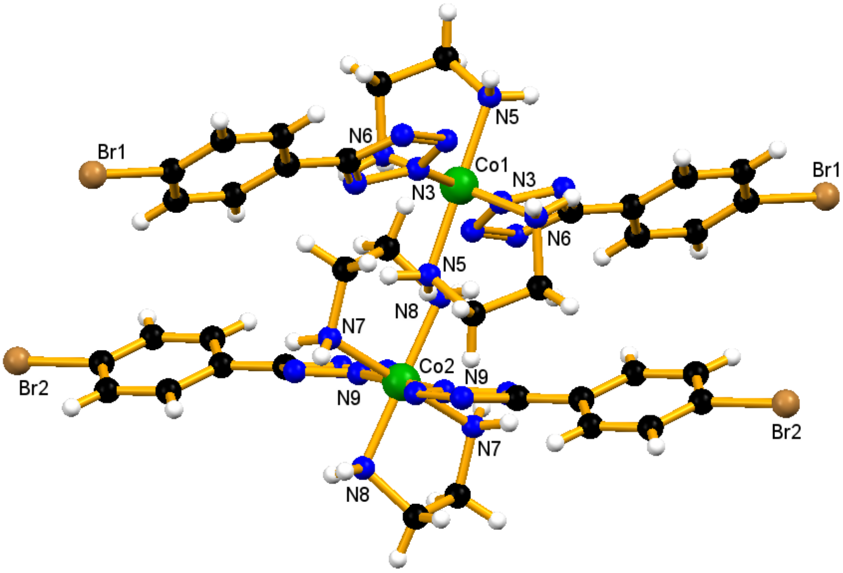


Fig. 8 View of compound ***trans*-4** having two crystallographically independent unit.

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