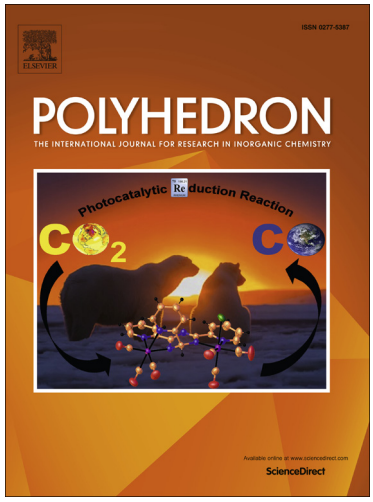

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Synthesis, spectral and structural characterization of cobalt(III) dithiocarbamato complexes: catalytic application for the solvent free enamination reaction

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ABSTRACT

The syntheses, spectral, structural and catalytic properties of some new cobalt(III) complexes, $[Co(mpcdt)_3]$ (**1**), $[Co(ppcdt)_3]$ (**2**) and $[Co(mppcdt)_3]\cdot 0.25CHCl_3$ (**3**), derived from 4-methyl piperazine-1-carbodithioate (mpcdt), 4-phenyl piperazine-1-carbodithioate (ppcdt) and 4-(2-methoxyphenyl) piperazine-1-carbodithioate (mppcdt) have been described. A series of β-enaminoesters and β-enaminones were obtained in about 90 % yield by the reactions of β-ketoesters and 1,3-diketones with aliphatic and aromatic amines using 1-2 mole % of the above cobalt(III) complexes as catalysts and these have been characterized by NMR, GC-MS and X-ray crystallography. Complexes **1**, **2** and **3** are stabilized by intermolecular C-H···S interactions, leading to the formation of supramolecular architectures. Thermogravimetric analysis of complexes **1** and **2** have been investigated by TG-DTA, which indicate that cobalt sulfide is formed as the final product.

Keywords: Dithiocarbamato complexes; Co(III) Catalysts; Solvent free enamination reaction; Thermal studies; Single crystal X-ray structure.

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1. INTRODUCTION

Transition metal complexes of dithiocarbamates have attracted the attention of workers in coordination chemistry due to their molecular electrical conductivity, optical and magnetic properties and applications as single source precursors for the preparation of nano particle metal sulfides. They also find applications in industry as rubber vulcanization accelerators, flotation agents in metallurgy, petroleum additives and are of importance in biological processes [1-11]. Dithiocarbamates have a wide range of applications in the fields of medicine, industry and agriculture and as antioxidants for increasing the longevity and photo-stability of a variety of polymers, oils and other materials [12]. Several dithiocarbamates and N-substituted dithiocarbamato complexes and their salts have been used as agrochemicals, mainly due to their high efficiency in controlling plant fungal diseases with relatively low toxicity [13,14]. We have explored the possibility of Co(III) dithiocarbamato complexes in chemical organic transformation reactions as catalysts because cobalt exhibits variable oxidation states, it is less expensive than other transition metals and is easily handled.

Enamination of 1,3-dicarbonyl and keto-esters to β-enamino ketones and β-enamino esters are important organic transformations because they are used as intermediates in the synthesis of heterocyclic compounds [15]. Several homogeneous catalysts such as $Ca(CF_3COO)_2$, $BF_3{:}OEt_2$, $Zn(ClO_4)_2{\cdot}6H_2O$, ceric ammonium nitrate and $Bi(OTf)_3$ [16] have been reported for the enamination of 1,3-dicarbonyl compounds, but they suffer from drawbacks associated with homogeneous catalysis. The versatility of enaminones is mainly due to their promptness to both electrophilic and nucleophilic attack [17]. For this reason, they have been used in the synthesis of various heterocyclic [18,19], natural products [20] and hence several methodologies have recently been developed for their synthesis [21], representing great

achievements compared to the original procedures [22]. The use of solid supports, ionic liquids and different types of catalysts has been found to be effective. The reactions of open-chain piperazine-containing ligands with metal ions such as palladium, nickel, copper, cobalt and iron yield complexes of different coordination geometries, depending on the coordinated metal, which further act as catalysts [23-27]. However, these catalysts are not reusable and the use of NaOtBu as a base requires the use of dried toluene and an inert atmosphere. In view of the above, we have synthesized new cobalt(III) dithiocarbamato complexes and examined their catalytic behaviour towards the formation of β-enaminoesters/β-enaminones by the reactions of β-ketoesters/1,3-diketones with aliphatic/aromatic amines. The cobalt(III) dithiocarbamato complexes used as catalysts and the reaction products obtained by the enamination reactions involving C-N bond formation have been authenticated and characterized by the crystal structures of some representative compounds.

2. Experimental

2.1. Chemicals and starting materials

Commercial reagents were used without further purification and all experiments were carried out in an open atmosphere. 1-Methyl piperazine, 1-phenyl piperazine, 4-(2-methoxyphenyl) piperazine (Sigma Aldrich), CS_2 (SD Fine Chemicals) and KOH (Qualigens) were used as received. The solvents were dried and distilled before use following the standard procedures.

2.2. Physical measurements

Carbon, hydrogen, nitrogen and sulfur contents were estimated on a CHN Model CE-440 Analyser and on an Elementar Vario EL III Carlo Erba 1108. The electronic spectra were recorded on a SHIMADZU 1700 UV-vis spectrophotometer. IR spectra were recorded in the

4000-400 cm^{-1} region as KBr pellets on a Varian Excalibur 3100 FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d_6 on a JEOL AL300 FT-NMR spectrometer using TMS as an internal reference. Thermogravimetric-differential thermal analyses (TG-DTA) were completed on a Perkin Elmer-STA 6000 thermal analyzer at a heating rate of 15 °C/min in a N_2 atmosphere. Gas chromatogram-mass spectral data were obtained on a quadrupole Perkin Elemer Clarus 500 MS coupled to a Perkin Elemer Clarus 500 GC with Elite-1 column and the mass detector was operated at 70 eV.

2.3. X-ray crystallography

The X-ray data collection for complexes **1**, **2**, **3** and compound **3b** were performed on an Oxford Diffraction Gemini diffractometer equipped with CrysAlis Pro., using a graphite monochromated Mo Kα (λ = 0.71073 Å) radiation source. The structures were solved by direct methods (SHELXL-2008) and refined against all data by full matrix least-squares on F^2 using anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen atoms were included in the refinement at geometrically ideal positions and refined with a riding model [28]. The MERCURY package and ORTEP-3 programs were used for generating the molecular structures [29,30].

2.4. Syntheses of potassium 4-methyl piperazine [K(mpcdt)], 4-phenyl piperazine [K(ppcdt)] and 4-(2-methoxy phenyl) piperazine [K(mppcdt)]-1 carbodithioates

The potassium salts of 4-methyl piperazine/4-phenyl piperazine/4-(2-methoxy phenyl) piperazine-1-carbodithioate were prepared by adding CS_2 (1.8 mL, 20 mmol) dropwise to a suspension of 1-methyl piperazine (2.00 mL, 20 mmol), 1-phenyl piperazine (3.26 mL, 20 mmol) and 1-(2-methoxyphenyl) piperazine (3.55 mL, 20 mmol) in methanol (20 mL) in the presence of potassium hydroxide (1.2 g, 20 mmol). The reaction mixtures were stirred continuously for 30

min under cold conditions and the separated white solids were filtered, washed with EtOH, dried under reduced pressure and recrystallized from a MeOH-$CHCl_3$ mixture (50:50 v/v).

2.4.1 [K(mpcdt)]: Yield: 70 %; m.p. 478 K. Anal. Found: C, 33.50; H, 5.15; N, 13.08; S, 29.80 %. Anal. Calc. for $C_6H_{11}N_2S_2K$ (215.00): C, 33.48; H, 5.11; N, 13.02; S, 29.76 %. IR (KBr, ν cm^{-1}): ν(C-N) 1469; ν(C=S) 970. ^{1}H NMR (DMSO-d_6; δ ppm): 4.38 (s, 3H, CH_3), 2.20-3.06 (m, 8H, CH_2). ^{13}C NMR (DMSO-d_6; δ ppm): 200.10 (C=S), 154.05 (C-N), 51.80-54.25 (CH_2), 45.25 (CH_3).

2.4.2 [K(ppcdt)]: Yield: 70 %; m.p. 475 K. Anal. Found: C, 47.79; H, 4.73; N, 10.11; S, 23.20 %. Anal. Calc. for $C_{11}H_{13}N_2S_2K$ (276.42): C, 47.80; H, 4.68; N, 10.12; S, 23.25 %. IR (KBr, ν cm^{-1}): ν(C-N) 1415; ν(C=S) 923. ^{1}H NMR (DMSO-d_6, δ ppm): 6.85-7.24 (m, 3H, phenyl ring), 3.20-4.54 (m, 8H, CH_2). ^{13}C NMR (DMSO-d_6, δ ppm): 209.57 (C=S), 150.86 (C-N), 116.2-129.2 (phenyl ring), 44.93-50.37 (CH_2).

2.4.3 [K(mppcdt)]: Yield: 72 %; m.p. 458 K. Anal. Found: C, 47.06; H, 4.90; N, 9.11; S, 20.94 %. Anal. Calc. for $C_{12}H_{15}N_2OS_2K$ (306.44): C, 47.03; H, 4.92; N, 9.13; S, 20.92 %. IR (KBr, ν cm^{-1}): ν(C-O) 1503; ν(C-N) 1463; ν(C=S) 928. ^{1}H NMR (DMSO-d_6, δ ppm): 6.85-7.25 (m, 3H, phenyl ring), 3.88 (s, 3H, CH_3), 3.08-3.46 (m, 8H, CH_2). ^{13}C NMR (DMSO-d_6, δ ppm): 209.56 (C=S), 152.20 (C-N), 111.12-123.68 (phenyl ring), 44.65-55.39 (CH_2).

*2.5. Syntheses of [Co(mpcdt)$_3$] (**1**), [Co(ppcdt)$_3$] (**2**) and [Co(mppcdt)$_3$]·0.25$CHCl_3$* (**3**)

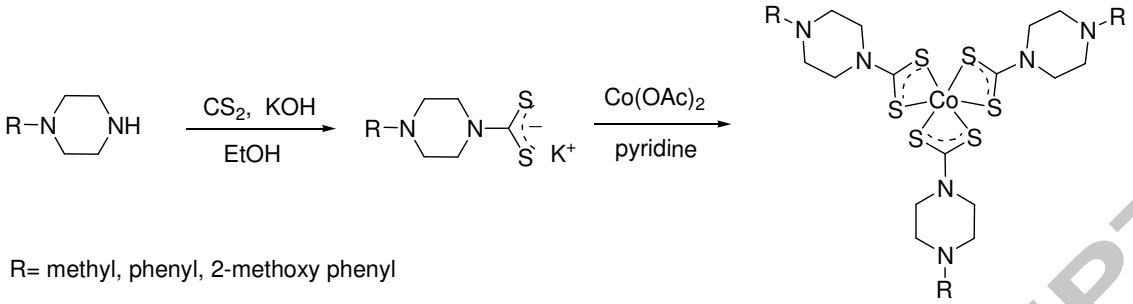
$Co(OAc)_2$ (0.177 g, 1 mmol) and each of [K(mpcdt)] (0.645 g, 3 mmol), [K(ppcdt)] (0.981 g, 3 mmol) and [K(mppcdt)] (1.071 g, 3 mmol) were dissolved separately in 10-20 mL methanol, mixed together and stirred for 1 h. The green solids which separated were filtered, washed successively with an ethanol:water mixture (50:50, v/v) and air dried. The solid compounds were suspended in methanol, a few drops of pyridine were added and the mixture

was warmed. The resulting clear green solutions were filtered off and kept for crystallization. Green colored single crystals of complexes **1**, **2** and **3**, suitable for X-ray analyses, were obtained by slow evaporation of the above solutions over a period of 10-15 days (Scheme 1).

*2.5.1 [Co(mpcdt)$_3$] (**1**):* Yield: 0.65 g, 72 %; m.p. 438 K; Anal. Found: C, 36.89; H, 5.66; N, 14.39; S, 32.87 %. Calc. for $C_{18}H_{33}CoN_6S_6$ (584.79): C, 36.93; H, 5.64; N, 14.36; S, 32.83 %. IR (KBr, ν cm^{-1}): ν(C-N) 1487; ν(C-S) 996; ν(M-S) 521; ^{1}H NMR (DMSO-d$_6$, δ ppm): 3.90 (s, 3H, CH_3), 2.47-2.32 (m, 8H, CH_2). ^{13}C NMR (DMSO-d$_6$, δ ppm): 203.06 (C=S), 152.20 (C-N), 42.34-44.42 (CH_2), 38.16 (CH_3).

*2.5.2 [Co(ppcdt)$_3$] (**2**):* Yield: 0.63 g, 68 %; m.p. 463 K; Anal. Found: C, 51.39; H, 5.06; N, 10.85; S, 24.97 %. Calc. for $C_{33}H_{39}CoN_6S_6$ (770.99): C, 51.36; H, 5.05; N, 10.89; S, 24.90 %. IR (KBr, ν cm^{-1}): ν(C-N) 1415; ν(C=S) 923; ν(M-S) 424. ^{1}H NMR (DMSO-d$_6$, δ ppm): 6.85-7.24 (m, 3H, phenyl ring), 3.20-4.54 (m, 8H, CH_2). ^{13}C NMR (DMSO-d$_6$, δ ppm): 209.57 (C=S), 150.86 (C-N), 116.2-129.2 (phenyl ring), 44.93-50.37 (CH_2).

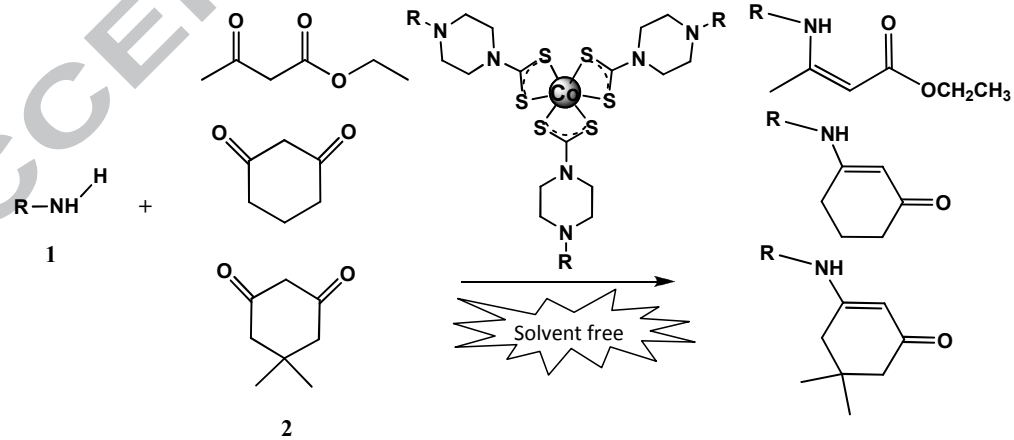
*2.5.3 [Co(mppcdt)$_3$]·0.25CHCl$_3$ (**3**):* Yield: 0.73 g, 76 %; m.p. 573 K; Anal. Found: C, 48.78; H, 5.06; N, 9.48; S, 21.57 %. Calc. for $C_{36}H_{45}CoN_6O_3S_6\cdot 0.25(CHCl_3)$ (890.91): C, 48.82; H, 5.07; N, 9.42; S, 21.55 %. IR (KBr, ν cm^{-1}): ν(C-O) 1498; ν(C-N) 1433; ν(C=S) 925; ν(M-S) 424. ^{1}H NMR (DMSO-d$_6$, δ ppm): 6.90-7.25 (m, 3H, phenyl ring), 3.8-4.08 (m, 8H, CH_2), 3.13 (s, 3H, CH_3). ^{13}C NMR (DMSO-d$_6$, δ ppm): 204.34 (C=S), 152.16 (C-N), 111.28-123.77 (phenyl ring), 45.49-55.44 (CH_2).



Scheme 1. Preparation of the ligands and their complexes, $[Co(mpcdt)_3]$ (**1**), $[Co(ppcdt)_3]$ (**2**) and $[Co(mppcdt)_3]\cdot 0.25CHCl_3$ (**3**)

2.6. General procedure for the synthesis of the β-enaminones and β-enaminoesters

The β-ketoester (1.2 mmol) or 1,3-diketone (1.2 mmol) was added to a mixture of the aromatic amine (1 mmol) or benzylamine (1 mmol) and 1 mol % of the cobalt catalyst under solvent free conditions. The reaction mixture was stirred at room temperature for 30 min. After the specified reaction time, the reaction mixture was extracted with EtOAc. The solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (hexane/EtOAc, 90:10) to afford the pure products (Scheme 2) (**3a-l**). All the compounds, except **3h**, are reported in the literature, so they were characterized by their melting points and spectral analyses.



Scheme 2. Enamination reaction of 1,3-dicarbonyl and β-ketoesters with amines

Characterization data of the compounds

*2.6.1 3-(Benzylamino)cyclohex-2-enone (**3a**)*: ^{1}H NMR ($CDCl_3$, δ ppm): 2.02-2.04 (m, 8H), 4.21 (s, 2H), 5.01 (s, 1H), 5.81 (s, 1H), 6.97-7.70 (m, 3H), 8.68 (s, 1H).

*2.6.2 3-(Phenylamino)cyclohex-2-enone (**3b**):* White solid; mp 457 K, GC-MS $[M+H]^{+}_{2}$: 377. ^{1}H NMR ($CDCl_3$, δ ppm): 2.04 (d, 2H), 2.35 (d, 2H), 2.49 (d, 2H), 5.57 (s, 1H), 6.28 (s, 1H), 7.13-7.32 (m, 3H). ^{13}C NMR ($CDCl_3$, δ ppm): 21.83, 29.83, 36.46, 100.08, 123.90, 125.60, 141.83, 148.34, 161.76.

*2.6.3 Ethyl 3-(benzylamino)but-2-enoate (**3c**):* ^{1}H NMR ($CDCl_3$, δ ppm): 1.19 (t, 3H), 1.91 (s, 3H), 4.05 (q, 2H), 4.61 (s, 2H), 6.61 (s, 1H), 6.99-7.23 (m, 5H), 10.29 (s, 1H). ^{13}C NMR ($CDCl_3$, δ ppm): 14.51, 29.65, 45.94, 58.81, 86.09, 124.38, 124.87, 128.99, 129.22, 139.31, 158.89.

*2.6.4 Ethyl 3-(phenylamino)butanoate (**3d**)*: ^{1}H NMR ($CDCl_3$, δ ppm): 1.06 (t, 2H), 2.29 (s, 3H), 3.37 (s, 1H), 3.87 (s, 1H), 4.16 (q, 3H), 6.73-7.46 (m, 5H). ^{13}C NMR ($CDCl_3$, δ ppm): 14.08, 22.43, 40.93, 82.99, 132.35, 133.09, 137.80, 152.46, 154.57.

*2.6.5 Ethyl 3-(2-methylpiperidin-1-yl)but-2-enoate (**3e**):* ^{1}H NMR ($CDCl_3$, δ ppm): 0.97 (s, 3H), 1.41-1.71 (m, 6H), 1.56 (t, 3H), 2.27 (s, 3H), 3.44-3.54 (m, 2H), 4.19 (q, 2H), 4.94 (s, 1H).

*2.6.6 3-(Benzylamino)-5,5-dimethylcyclohex-2-enone (**3f**):* ^{1}H NMR ($CDCl_3$, δ ppm): 1.25 (d, 2H), 1.28 (d, 2H), 1.44 (d, 2H), 4.62 (s, 1H), 6.28 (s, 1H), 7.43-6.47 (m, 4H), 8.03 (s, 1H). ^{13}C NMR ($CDCl_3$, δ ppm): 19.41, 34.63, 41.91, 141.83, 108.61, 113.86, 124.38, 137.76, 147.73, 147.83, 158.35, 196.75.

*2.6.7 3-(Benzylamino)-5,5-dimethylcyclohex-2-enone (**3g**):* ^{1}H NMR ($CDCl_3$, δ ppm): 0.91 (m, 6H), 2.03 (s, 2H), 3.77 (s, 1H), 4.19 (s, 1H), 4.43 (s, 1H), 7.31-7.52 (m, 3H).

*2.6.8 5,5-Dimethyl-3-(pyridin-2-ylamino)cyclohex-2-enone (**3h**):* Yellow solid; m.p. 451 K. GC-MS [M^+]: 216. ^{1}H NMR ($CDCl_3$, δ ppm): 1.08 (s, 6H), 2.20 (s, 2H), 2.34 (s, 2H), 5.56 (s, 1H), 6.82 (s, 1H), 7.33-7.12 (m, 4H). ^{13}C NMR ($CDCl_3$, δ ppm): 28.30, 32.78, 43.44, 50.24, 98.27, 123.84, 125.47, 129.26, 138.16, 160.71, 160.76, 198.02.

*2.6.9 5,5-Dimethyl-3-(phenylamino)cyclohex-2-enone (**3i**):* ^{1}H NMR ($CDCl_3$, δ ppm): 1.02 (m, 6H), 2.26 (s, 2H), 2.02 (s, 2H), 4.14 (s, 1H), 7.70-6.97 (m, 3H), 12.51 (s, 1H). ^{13}C NMR ($CDCl_3$, δ ppm): 29.68, 30.04, 35.40, 45.12, 46.06, 87.20, 126.20, 138.91, 141.64, 147.16, 159.21, 191.80.

*2.6.10 3-(Piperidin-1-yl)cyclohex-2-enone (**3j**):* ^{1}H NMR ($CDCl_3$, δ ppm): 1.61-2.00 (m, 6H), 2.26 (t, 2H), 2.99 (t, 2H), 3.34 (t, 2H), 3.36 (t, 2H), 4.50 (s, 1H).

*2.6.11 Ethyl 3-(piperidin-1-yl)but-2-enoate (**3k**):* ^{1}H NMR ($CDCl_3$, δ ppm): 1.28 (t, 3H), 1.89-1.97 (m, 6H), 2.28 (s, 3H), 3.45 (t, 2H), 3.47 (t, 2H), 4.20 (q, 2H), 7.32 (s, 1H). ^{13}C NMR ($CDCl_3$, δ ppm): 13.96, 19.26, 21.06, 30.01, 46.67, 50.01, 61.27, 89.75, 126.59, 127.21, 128.65, 167.04, 200.60.

*2.6.12 5,5-Dimethyl-3-(piperidin-1-yl)cyclohex-2-enone (**3l**):* ^{1}H NMR ($CDCl_3$, δ ppm): 1.04 (m, 6H), 1.62-1.77 (m, 6H), 1.95-2.12 (m, 4H), 2.99-3.01 (m, 4H), 6.31 (s, 1H).

3. Results and discussion

The potassium salts of the new dithiothiocarbomato ligands 4-methyl piperazine-1-carbodithioate [K(mpcdt)], 4-phenyl piperazine-1-carbodithioate [K(ppcdt)] and 4-(2-methoxyphenyl) piperazine-1-carbodithioate [K(mppcdt)] form the complexes [Co(mpcdt)$_3$] (**1**), [Co(ppcdt)$_3$] (**2**) and [Co(mppcdt)$_3$]·0.25$CHCl_3$ (**3**), respectively in the presence of warm pyridine. It is observed that Co(II) is converted to Co(III) by aerial oxidation in the presence of the dithio ligand, forming the [Co(carbodithioate)$_3$] complexes. It has already been reported that

$VO(acac)_2$, zinc nanoparticles, $Ca(CF_3COO)_2$ based and other catalysts catalyse the formation of β-enaminones [31,32]. In these reactions, β-enaminoesters/β-enaminones are obtained from β-ketoesters and 1,3-diketones with aliphatic/aromatic amines using 10 mol% of $VO(acac)_2$/$Ca(CF_3COO)_2$ as a catalyst. The corresponding products were obtained in 82-90 % yield with a low environmental impact, whereas the same reaction requires 80 ^oC in the presence of zinc nanoparticles as a catalyst. Herein, we demonstrate that cobalt(III) based complexes catalyse the enamination reactions of 1,3-dicarbonyls and β-ketoesters with amines in a very efficient manner under solvent free conditions at room temperature.

*3.1. Catalytic activity of complexes **1**, **2** and **3***

The presence of the Lewis acidic Co(dithiocarbamato)$_3$ complexes, which are able to provide labile sites during reactions of the complexes, has resulted in their possible role in organic transformation reactions. The enamination reaction, which requires the nucleophilic addition of an amine to the carbonyl group mediated by a Lewis acidic center such as the Co(dithiocarbamato)$_3$ complexes, has been successfully carried out, demonstrating the possible catalytic behaviour of the present complexes (Table 1)**.**

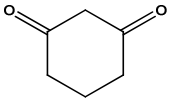
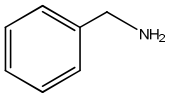
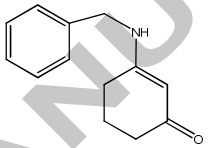
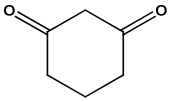
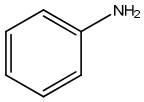
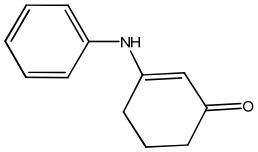
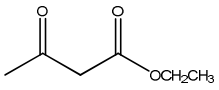
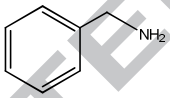
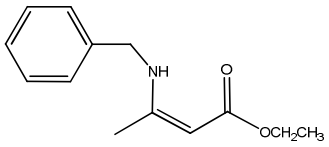
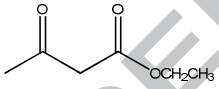
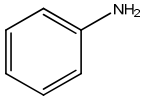
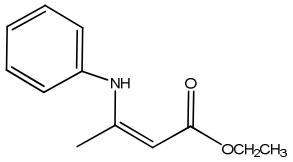
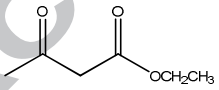
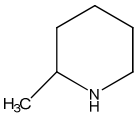
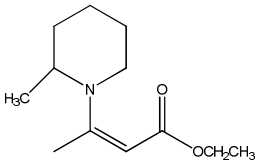
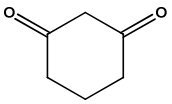
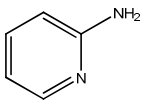
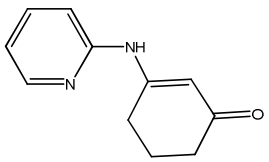
Table 1. Optimization studies of Co(dithiocarbamato)$_3$ catalysed enamination reactions of 1, 3-dicarbonyls and β-ketoesters with amines [a]

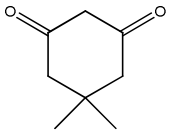
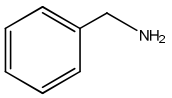
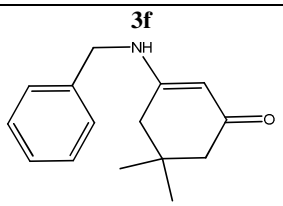
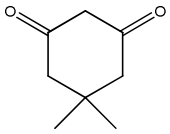
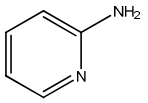
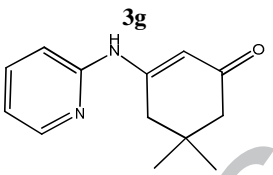
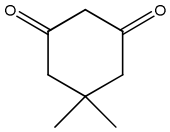
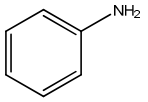
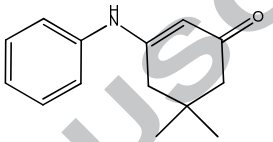
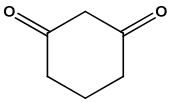
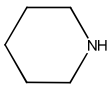
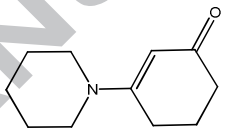
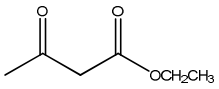
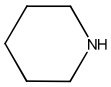
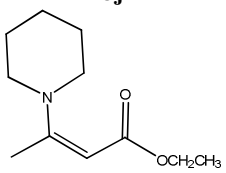
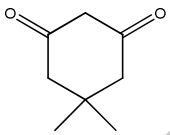
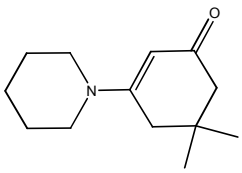
Entry	Catalyst used	Catalyst amount in mol %	Reaction time (min)	Product	Yield[b] %
1	No catalyst	-	4 days	**3d**	50
2	Co(III) complex	1	30	**3d**	82
3	Co(III) complex	2	25	**3d**	85
4	Co(III) complex	3	20	**3d**	88
5	Co(III) complex	5	15	**3d**	95
6	Co(III) complex	10	15	**3d**	93

[a] The reactions were carried out with ethyl acetoacetate (2.4 mmol) and aniline (2.0 mmol)
[b] Isolated yield.

In the above reactions, the 1,3-dicarbonyls and β-ketoesters were treated with amines in the presence of 1-2 mol % of $[Co(mpcdt)_3]$ (**1**), $[Co(ppcdt)_3]$ (**2**) and $[Co(mppcdt)_3]\cdot 0.25CHCl_3$ (**3**) under solvent free conditions for 30 min at room temperature; the corresponding β-enaminones and β-enaminoesters were obtained in about 90 % yield (Table 2, entries 1-12).

Table 2. Catalytic activity of $[Co(mpcdt)_3]$ (**1**), $[Co(ppcdt)_3]$ (**2**) and $[Co(mppcdt)_3]\cdot 0.25CHCl_3$ (**3**) for the preparation of β-enaminones and β-enaminoesters by the reaction of 1,3-dicarbonyls and β-ketoesters with amines[a]

Entry	1	2	Time (min)/ Catalyst	Product (**3**)	Yield[b] (Complex)
1			35 **1**, **2**, **3**	 **3a**	90
2			40 **1**, **3**	 **3b**	85
3			40 **1**, **3**	 **3c**	88
4			30 **1**, **2**, **3**	 **3d**	80
5			40 **1**, **2**, **3**	 **3e**	88
6			40 **1**, **2**, **3**		80

Entry	1	2	Time (min)/ Catalyst	Product (3)	Yield[b] (Complex)
7			35 **1**, **2**	**3f** 	90
8			35 **1**, **3**	**3g** 	85
9			45 **1**, **2**, **3**	**3h** 	85
10			40 **1**, **2**	**3i** 	90
11			30 **1**, **2**	**3j** 	85
12			30 **1**, **2**, **3**	**3k** 	80
				3l	

[a] The reactions were performed using a β-ketoester (1.2 mmol) or 1,3-diketone (1.2 mmol) and an aromatic amine (1 mmol), aliphatic amine (1 mmol) or benzylamine (1 mmol).
[b] Isolated yield.

The reaction products have been characterized by melting points and NMR studies. The compound 2 3-(phenylamino)cyclohex-2-enone (**3b**) has also been characterized by GC-MS and single crystal X-ray diffraction data. It has been observed that the cobalt(III) complexes **1**, **2** and **3**, bearing a strongly π-accepting ligand, act as an efficient catalyst for the enamination reaction

of 1,3-dicarbonyls/β-ketoesters with amines and related compounds. Notable features of these complexes are their outstanding stability in air and moisture in the solid state. Virtually no decomposition of the complexes has been detected after extended (6 months) exposure to air. The X-ray crystal structure of the complexes indicates that this may be due to the effective shielding of the cobalt atom by three dithiocarbomato ligands and their stabilization by intermolecular C-H···S hydrogen bonding. Complexes **1**, **2** and **3** are able to promote the reactions between an amine and the carbonyl moiety containing various substituents. Without the complexes the reaction did not proceed at all, supporting the possible Lewis acid catalysed activity of the networks. Further, when the catalyst is filtered off, the reaction was not promoted any more. A control experiment using the building blocks of the complexes also did not result in any product formation. However, the homogeneous reaction with a cobalt complex as a catalyst resulted in <80% conversion, demonstrating the enhanced catalytic activity of networks of complexes, like the heterogeneous conditions. These experiments clearly show that the soluble and catalytically active species are not eluted at all from the networks of complexes under the reaction conditions. Thus the reactions are expected to proceed by the heterogeneous catalysis of the networks.

*3.2. Thermogravimetric analysis of complexes **1** and **2***

The thermal properties of $[Co(mpcdt)_3]$ (**1**) were studied by TGA and DTA in the temperature range 30-800 ºC under a nitrogen atmosphere. The thermogravimetric analysis of complex **1** shows that it starts decomposing at 185 ºC and the thermogram exhibits two distinct decompositions steps at 185 and 386 ºC. The weight loss of 67.44 % in the temperature range 185 to 386 ºC could be ascribed to the loss of three methyl piperazine moieties (cal.: 65.08 %).

The second decomposition in the temperature range 386 to 789 ºC may be due to loss of the remaining organic moieties, after which cobalt sulfide is formed as the final residue, 14.55 %. The corresponding endo and exothermic peaks in the DTA were obtained at 232, 270, 500 and 650 ºC (Fig. 1).

The thermal properties of $[Co(ppcdt)_3]$ (**2**) were studied by TGA and DTA in the temperature range 30-900 ºC under a nitrogen atmosphere. Thermogravimetric analysis of complex **2** shows that it starts decomposing at 260 ºC and the thermogram exhibits two distinct decompositions steps at 260 and 326 ºC. The weight loss of 76.46 % in the temperature range 260 to 326 ºC could be ascribed to the loss of three phenyl piperazine moieties (cal.: 79.86 %). The second decomposition in the temperature range 326 to 900 ºC may be due to loss of the remaining organic moieties, after which cobalt sulfide is formed as the final residue, 12.9 %. The corresponding endo and exothermic peaks in the DTA were obtained at 245, 327, 640 and 810 ºC (Fig. 2).

3.3. Crystal structure determination

Figs. 3, 5, 7 and 9 show molecular structure diagrams of complexes **1**, **2**, **3** and **3b**, with the atom numbering schemes, and the structural refinement data related to complexes **1**, **2**, **3** and compound **3b** are listed in Table 3. Hydrogen bonding structures of compounds **1**, **2**, **3** and **3b** are shown in Figs. 4, 6, 8 and 10, respectively.

Table 3. Crystallographic data table of complexes $[Co(mpcdt)_3]$ (**1**), $[Co(ppcdt)_3]$ (**2**), $[Co(mppcdt)_3]\cdot 0.25CHCl_3$ (**3**) and compound **3b**

Compound	**1**	**2**	**3**	**3b**
Empirical formula	$C_{18}H_{33}CoN_6S_6$	$C_{33}H_{39}CoN_6S_6$	$C_{36}H_{45}CoN_6O_3S_6.0.25(CHCl_3)$	$C_{12}H_{13}NO$
Formula weight	584.79	770.99	890.91	187.23
T (K)	296(2)	293(2)	295(2)	293(2)
Λ (Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Trigonal	Monoclinic	Monoclinic	Monoclinic
Space group	R-3c	P 21/c	C 2/c	P 21/c
a (Å)	13.17(6)	15.21(5)	16.07(8)	6.12(7)
b (Å)	13.17(6)	6.23(3)	18.60(10)	11.17(12)
c (Å)	30.37(16)	41.96(2)	31.51(16)	14.44(10)
α (º)	90.00	90.00	90.00	90.00
β (º)	90.00	96.62(4)	105.00(6)	90.95(8)
γ (º)	120.00	90.00	90.00	90.00
V ($Å^3$)	4563.7(5)	3956.5(3)	9102.7(8)	988.60(17)
Z	6	4	8	4
D_{calc}(Mg m^{-3})	1.27	1.29	1.30	1.25
μ (mm^{-1})	0.99	0.78	0.73	0.08
F(000)	1836	1608	3716	357
Crystal size (mm^3)	0.30x0.27x0.25	0.30x0.27x0.24	0.37x0.25x0.18	0.37x0.27x0.24
θ range (º)	3.09-28.87	3.14-29.20	3.35-30.30	3.65- 29.07
Index ranges	-16≤ h ≤ 16 -12≤ k ≤15 -40≤ l ≤22	-19≤ h ≤19 -8≤ k ≤8 -56≤ l ≤56	-20≤ h ≤20 -25≤ k ≤24 -42≤ l ≤35	-4≤ h ≤8 -10≤ k ≤15 -17≤ l ≤19
Reflections collected	3336	21760	39509	1461
Independent reflections	1195	9198	11029	2654
Data/restraints/ parameters	1195/42/62	9198/0/443	11029/12/502	2654/0/127
Goodness-of-fit on F^2	1.170	1.043	1.05	0.82
Final R indices wR_2 [I>2σ(I)](R_{int})	0.06, 0.25	0.08, 0.18	0.07, 0.22	0.05, 0.18
Final R indices (all data)	0.08, 0.26	0.16, 0.22	0.12,0.28	0.090, 0.24
Largest diff. peak/hole (e $Å^{-3}$)	1.26, -0.51	0.48, -0.36	1.07, -0.91	0.40, -0.24

[a] $R_1 = \Sigma||F_o| - |Fc||\Sigma|F_o|$.

[b] $R_2 = [\Sigma w(|F^2_o| - |F^2_c|)^2/\Sigma w|F^2_o|^2]^{1/2}$.

*3.4. Crystal structure descriptions of complexes **1**, **2** and **3***

The coordination sphere of complexes **1**, **2** and **3** are fulfilled by two dithio-sulfur atoms from each of the three bidentate carbodithioate moieties. The formation of three four membered CS_2Co chelate rings, each with a bite angle of 76.71(7)º for complex **1**, 76.56(6)º for complex **2** and 76.33(5)º for complex **3**, represent a deviation from an ideal octahedral geometry. The Co-S bond distances for the three CS_2Co chelate rings are equal, being 2.2683(15) Å, for complex **1** but they are unequal for complexes **2** and **3**, being 2.2559(16), 2.2667(16), 2.2685(15), 2.2758(17), 2.2788(17) and 2.2864(16) Å for complex **2** and 2.2561(12), 2.2685(15), 2.2733(13), 2.2767(13) and 2.2778(13) Å (Table 4) for complex **3**. The Co-S distances are comparable to the bond lengths reported earlier for other similar cobalt dithio complexes, e.g. $[Co\{S_2CN(CH_2CH_2CH_2NMe_2)_2\}_3]$ [33]. The carbon-sulfur distances within the chelate rings are intermediate between single and double bond lengths. The average bond length, S(1)-C(1) = 1.704(5) Å for complex **1**, S(1)-C(1) = 1.704(6), S(2)-C(1) = 1.726(6), S(3)-C(12) = 1.724(5), S(4)-C(12) = 1.713(5), S(5)-C(23) = 1.704(6) and S(6)-C(23) = 1.712(5) Å for complex **2** and S(1C)-C(1C) = 1.720(4) and S(2C)-C(1C) = 1.699(5) Å (Table 4) for complex **3** suggest considerable delocalization of charge [34]. In the complexes, the chelate rings and the piperazine ring lie nearly in the same plane. The piperazine ring makes an extended coplanar system with two chelate rings.

Table 4. Interatomic distances (Å) and angles (°) for $[Co(mpcdt)_3]$ (**1**), $[Co(ppcdt)_3]$ (**2**) and $[Co(mppcdt)_3]\cdot 0.25CHCl_3$ (**3**)

$[Co(mpcdt)_3]$ (**1**)			
Bond lengths (Å)		Bond angles (°)	
Co(1)-S(1)	2.26(15)	S(1)-Co(1)-S(1)	76.71(7)
Co(1)-S(1)	2.26(15)	S(1)-Co(1)-S(1)	96.27(8)
		S(1)-Co(1)-S(1)	166.58(8)
$[Co(ppcdt)_3]$ (**2**)			

Co(1)-S(1)	2.26(16)	S(5)-Co(1)-S(1)	94.23(7)
Co(1)-S(3)	2.26(15)	S(5)-Co(1)-S(3)	169.08(7)
Co(1)-S(5)	2.25(16)	S(1)-Co(1)-S(2)	76.56(6)
$[Co(mppcdt)_3]\cdot 0.25CHCl_3$ (**3**)			
Co(1)-S(1A)	2.27(13)	S(1B)-Co(1)-S(2A)	95.09(5)
Co(1)-S(1B)	2.27(13)	S(2A)-Co(1)-S(1C)	167.16(5)
Co(1)-S(1C)	2.26(15)	S(1C)-Co(1)-S(2C)	76.33(5)

Table 5. Hydrogen bonding parameters for $[Co(ppcdt)_3]$ (**2**) and $[Co(mppcdt)_3]\cdot 0.25CHCl_3$ (**3**)

$[Co(ppcdt)_3]$ (**2**)					
D-H···A	D-H [Å]	H···A[Å]	D···A [Å]	∠ D-H···A [°]	Sym Operator
C20-H1···S5	0.93	2.95	3.61	129.29	1-x,-y,-z
C27-H28B···S6	0.97	2.28	3.82	168.10	-x,1-y,-z
$[Co(mppcdt)_3]\cdot 0.25CHCl_3$ (**3**)					
D-H···A	D-H [Å]	H···A[Å]	D···A [Å]	∠ D-H···A [°]	Sym Operator
C12A-H12A···S1C	0.96	2.85	3.79	165.3	-1/2+x,-1/2+y,z
C4A-H4AB···S1B	0.96	2.76	3.51	134.9	1-x,y,1.5-z
C9B-H9BA···S2C	0.93	2.86	3.77	167.74	-x,y,1.5-z

In the solid state, the complexes are stabilized via intermolecular C-H···S interactions between the dithio sulfur and hydrogen atoms of the piperazine ring (Fig. 4, 6 and 8, Table 5).

*3.5. Crystal structure descriptions of 3-(phenylamino)cyclohex-2-enone (**3b**)*

Fig. 9 shows the molecular structure diagram of 3-(phenylamino)cyclohex-2-enone (**3b**) with the atomic numbering scheme. The carbon nitrogen bond distance C7-N1 (1.346 Å) is shorter than C1-N1 (1.424 Å) because the C7 carbon is doubly and singly bonded to other two carbons, C8 and C12, whereas C1 is bonded to others two carbons, C6 and C2, involved in

delocalized π-bonding. Compound **3b** is stabilized *via* intermolecular N-H···O interactions between the NH hydrogen atom of the phenyl amine and the 2-enone oxygen atom of other unit of a 3-(phenylamino)cyclohex-2-enone molecule (Fig. 10).

4. Conclusion

New complexes, $[Co(mpcdt)_3]$ (**1**), $[Co(ppcdt)_3]$ (**2**) and $[Co(mppcdt)_3]\cdot 0.25CHCl_3$ (**3**), derived from 4-methyl piperazine-1-carbodithioate/4-phenyl piperazine-1-carbodithioate/4-(2-methoxyphenyl)piperazine-1-carbodithioates have been synthesized and characterized by single crystal X-ray. During complexation with the carbodithioate ligands, Co(II) is converted to Co(III) by aerial oxidation, forming distorted octahedral $[Co(carbodithioate)_3]$ complexes. In comparison with the reported metal catalysed enamination reactions of 1,3-dicarbonyls and ketoesters with amines, the present work offers an effiicient alternative catalytic system for the formation of a carbon-nitrogen bond. Most copper catalysed reactions usually require high catalyst loading and high reaction temperatures. The cobalt(III) catalysed reactions presented here employ simple dithio-piperazine ligands which offers a good complement to Pd(II), Ni(II) as well as Co(II) catalysed reactions in terms of low environmental impact, easy preparation, less cost and high activity, with a very low amount of catalyst loading. The new reaction system has the potential of using a cobalt(III) complex as a very user-friendly, inexpensive and efficient catalyst. TGA analysis of complexes **1** and **2** show that the complexes are stable up to 185 °C and undergo two step decompositions, leading to the formation of cobalt sulfide as the final product.

5. Supplementary material

CCDC 917700, 902647, 982764 and 962738 contain the supplementary crystallographic data for the complexes $[Co(mpcdt)_3]$ (**1**), $[Co(ppcdt)_3]$ (**2**), $[Co(mppcdt)_3]\cdot 0.25CHCl_3$ (**3**) and the

derivative **3b**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 IEZ, UK; fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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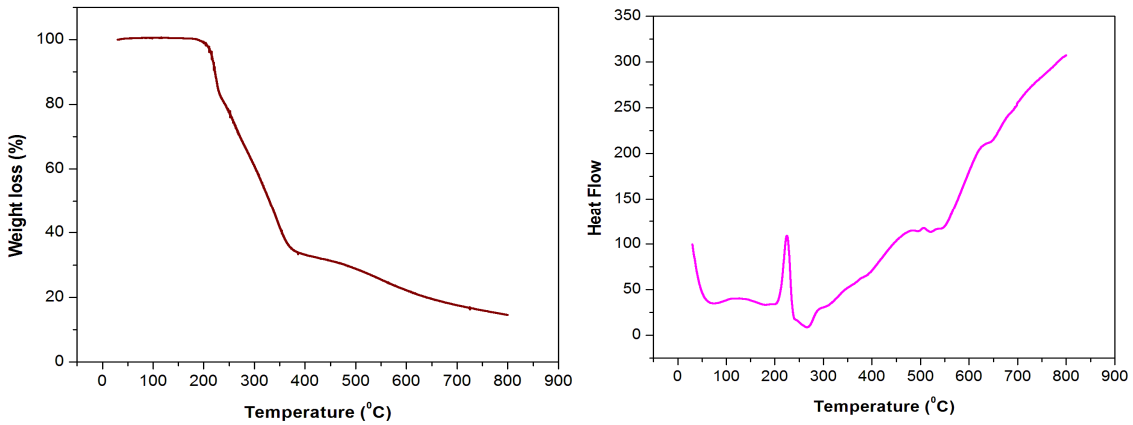


Fig. 1 (a) TGA; **(b)** DTA curve of $[Co(mpcdt)_3]$ (**1**)

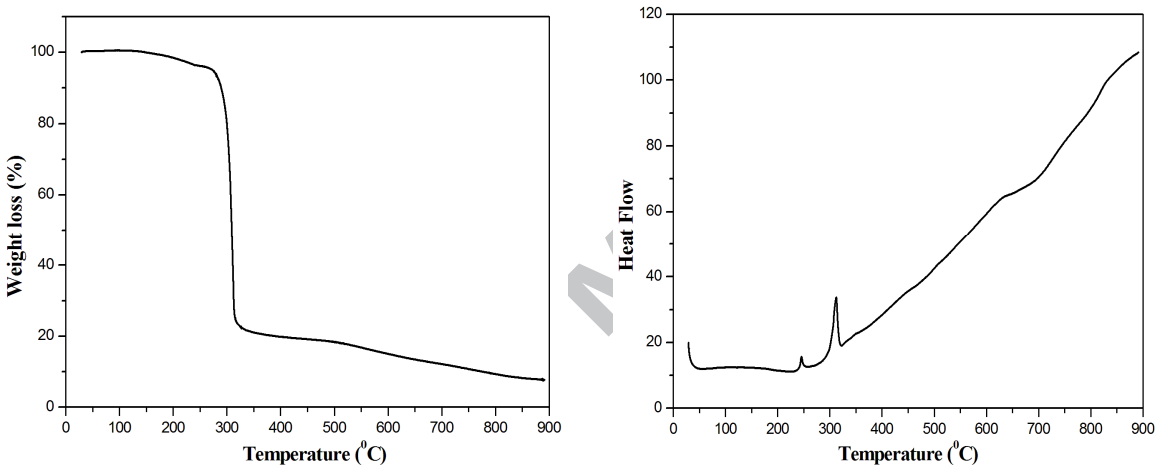


Fig. 2 (a) TGA; **(b)** DTA curve of $[Co(ppcdt)_3]$ (**2**)

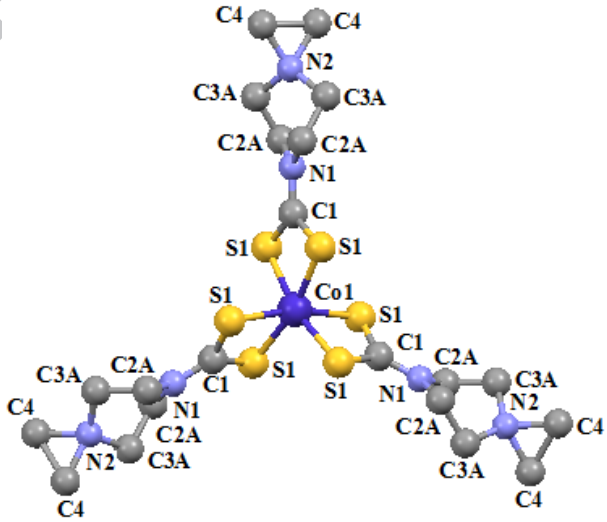


Fig. 3 Molecular structure of [Co(mpcdt)$_3$] (**1**) with the atomic numbering scheme at the 30% probability level

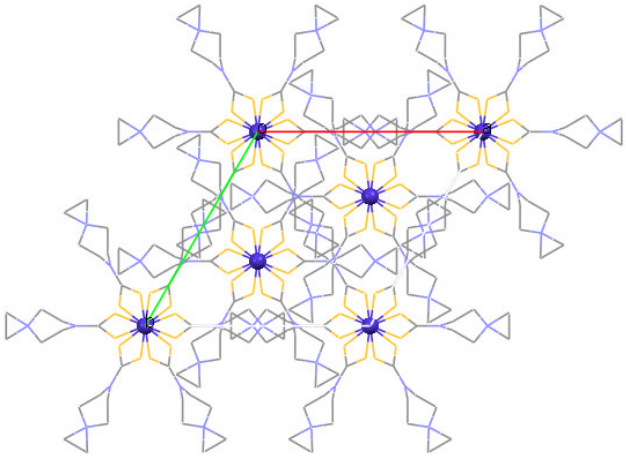


Fig. 4 C-H···S hydrogen bonding and packing diagrams of [Co(mpdtc)$_3$] (**1**)

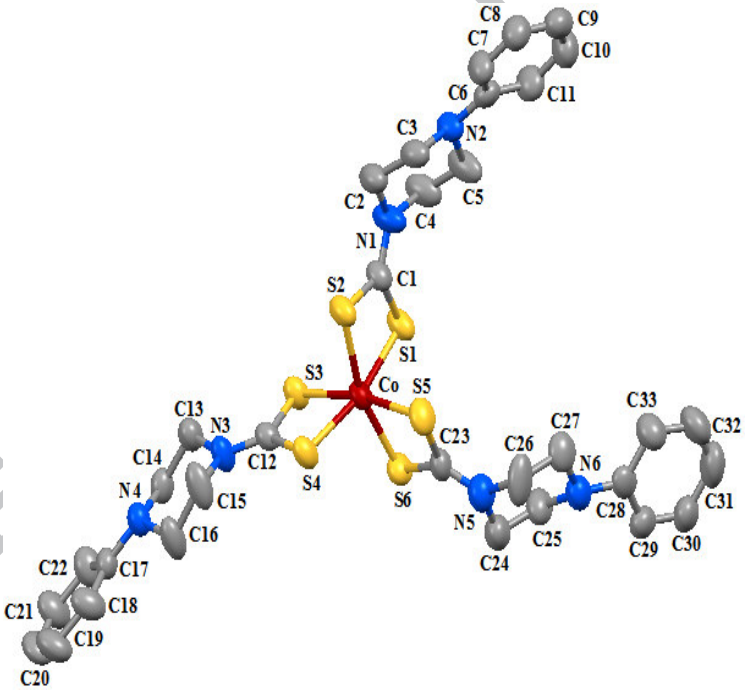


Fig. 5 Molecular structure of [Co(ppcdt)$_3$] (**2**) with the atomic numbering scheme at the 30% probability level

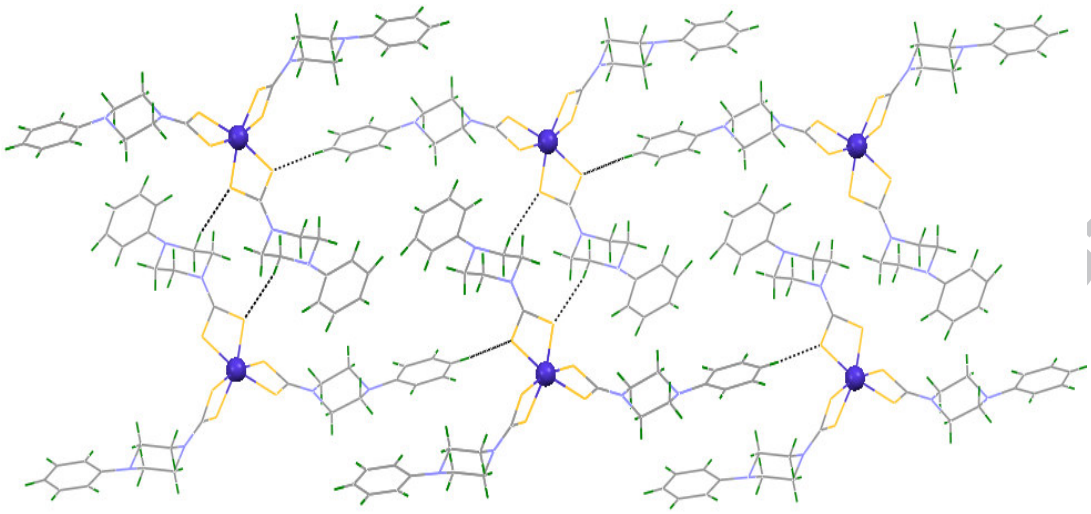


Fig. 6 C-H···S hydrogen bonding in [Co(ppdtc)$_3$] (**2**) leading to the formation of a supramolecular architecture

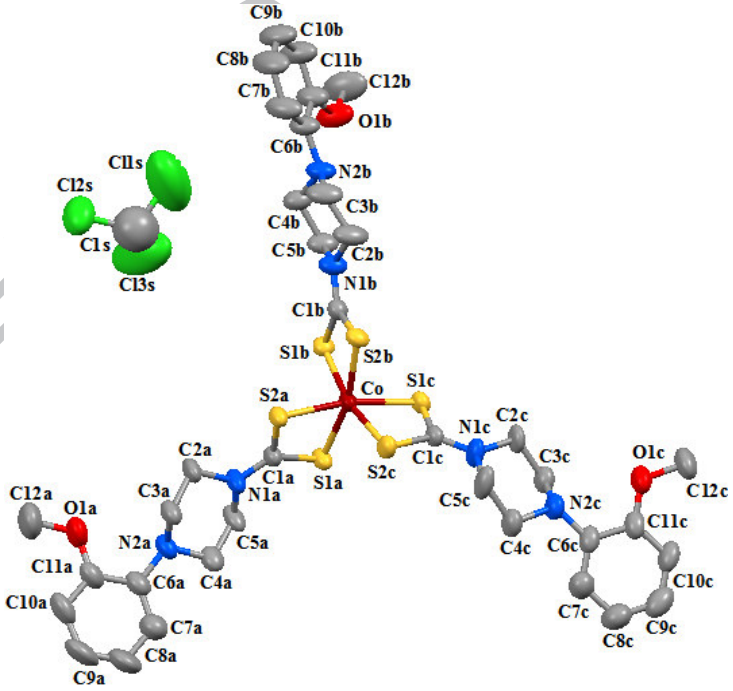


Fig. 7 Molecular structure of [Co(mppcdt)$_3$]·0.25($CHCl_3$) (**3**) with the atomic numbering scheme at the 30% probability level

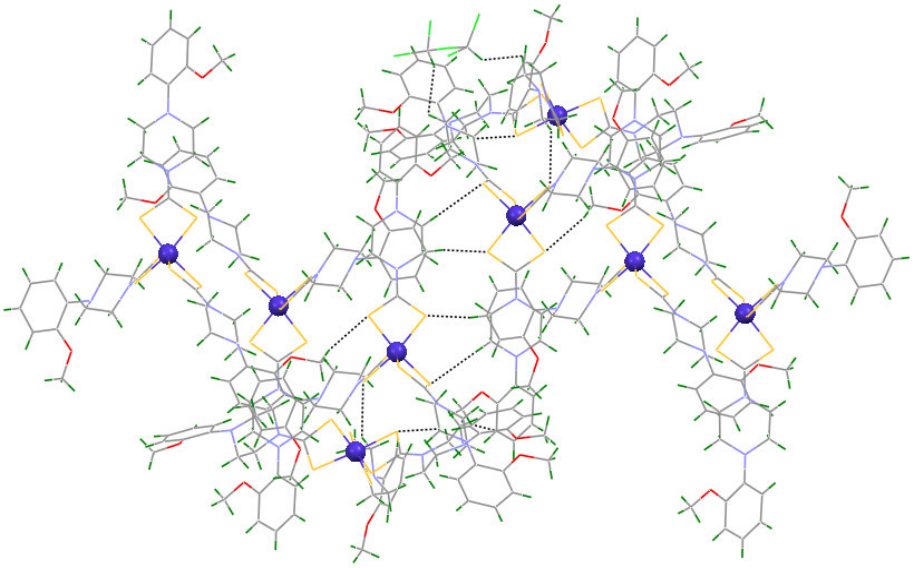


Fig. 8 C-H···S hydrogen bonding $[Co(mppdtc)_3]\cdot 0.25CHCl_3$ (**3**) leading to the formation of a supramolecular architecture.

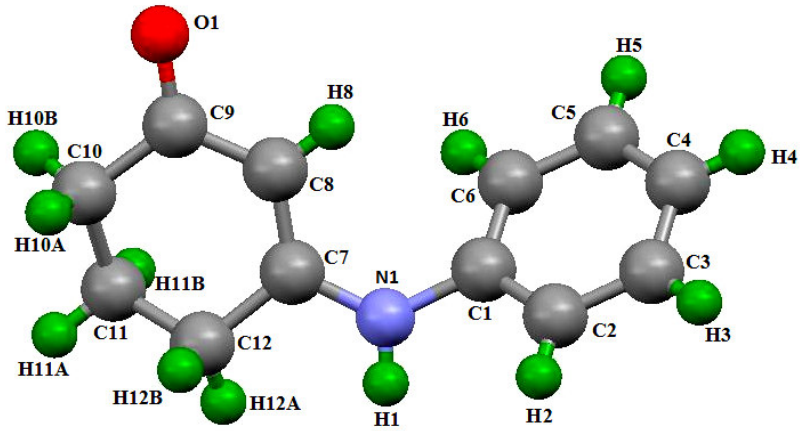


Fig. 9 Molecular structure of 2 3-(phenylamino)cyclohex-2-enone (**3b**) with the atomic numbering scheme at the 30% probability level

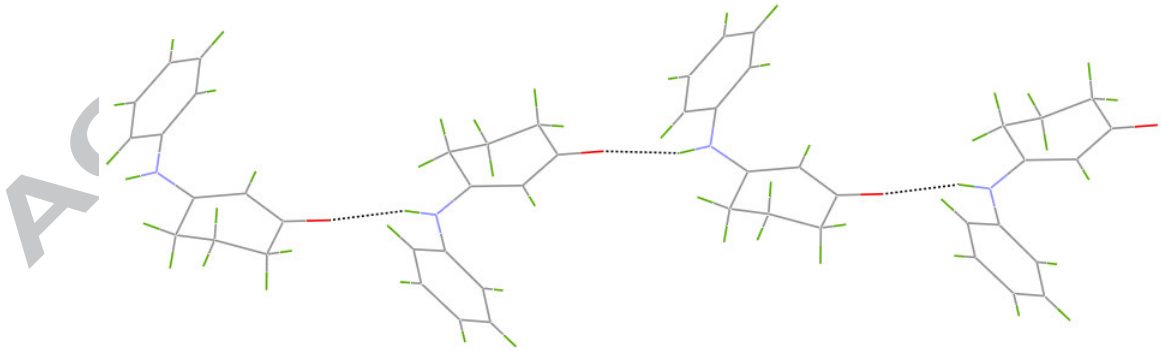
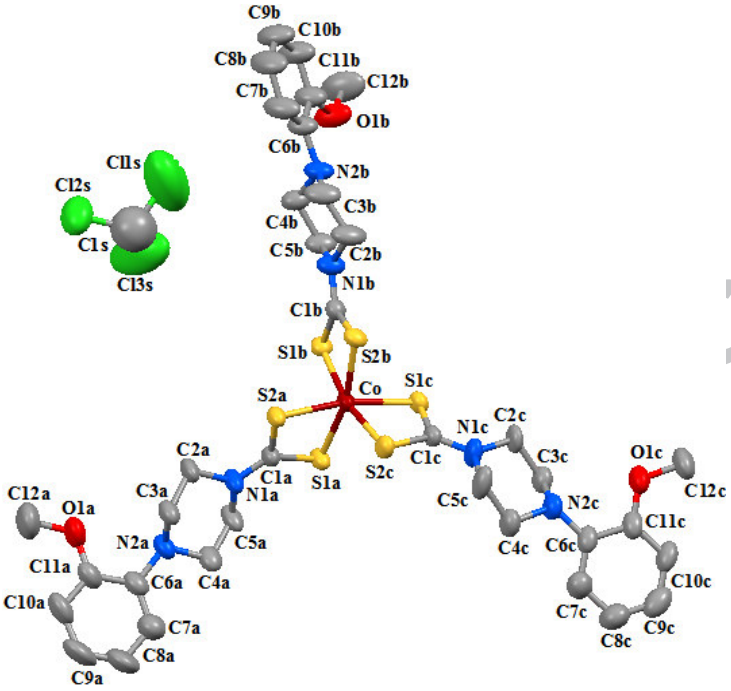


Fig. 10 Intermolecular N-H···O interactions in 2 3-(phenylamino)cyclohex-2-enone (**3b**) leading to a 1D-structure

Graphical Abstract (Picture)



Graphical Abstract (Synopsis)

Three new cobalt(III) complexes, $[Co(mpcdt)_3]$ (**1**), $[Co(ppcdt)_3]$ (**2**) and $[Co(mppcdt)_3]\cdot 0.25CHCl_3$ (**3**), of 4-methyl piperazine-1-carbodithioate (mpcdt), 4-phenyl piperazine-1-carbodithioate (ppcdt) and 4-(2-methoxyphenyl) piperazine-1-carbodithioate (mppcdt) have been synthesized and characterized by various physicochemical techniques. The catalytic properties of the above complexes have also been examined. A series of β-enaminoesters and β-enaminones were obtained by the reactions of β-ketoesters and 1,3-diketones with aliphatic and aromatic amines, using the above cobalt(III) complexes as catalysts, which have been characterized by NMR, GC-MS and X-ray crystallography. Thermogravimetric analysis of complexes **1** and **2** have been investigated by TG-DTA, which indicate that cobalt sulfide is formed as the final product.