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Piperazine-bridged homodinuclear transition metal complexes

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Piperazine-bridged transition metal complexes of the type [M(etdtc)]$_2$ppzdtc and [M^1(etdtc)$_2$]$_2$ppzdtc [where M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II), M^1 = Cr(III), Fe(III), etdtc = ($S_2NC_5H_{10}$) and ppzdtc = [$S_2C(NCH_2CH_2)_2CS_2$] have been synthesised and characterised by elemental analyses, magnetic susceptibility measurements, TGA/DSC, IR and electronic spectroscopy and conductivity measurements. The presence of only one (C–S) stretching frequency at around 1000 cm^{-1} supports symmetrical bonding of the dithiocarbamato-moiety. The low molar conductance value of the complexes in DMSO at 25 °C indicates their non-electrolytic behaviour. Thermogravimetric analysis showed only two-step, simple pyrolysis. The decomposition is generally exothermic, leading to the formation of metal sulfide as the final product. The complexes of divalent metal ions appear to be tetrahedral, excepting Cu(II) and Ni(II) which are square-planar, while those of trivalent metal ions are octahedral, which is also corroborated from their electronic spectra and magnetic moment data.

Keywords: piperazine, symmetrical dithiocarbamates, thermogravimetric analysis

Piperazine exists in chair or boat conformations, but usually the chair form is preferred as it is 17.2 kJ /mol more stable than the boat form.[1] However, the boat conformation is stabilised when the piperazine ring binds one metal ion through both the nitrogen atoms forming a bidentate chelate complex as in cis-[$PtCl_2(Me_2ppz)$][2] (where Me_2ppz = 1,4-dimethylpiperazine). Moreover, no such complex with Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) could be isolated as the piperazine ring is constrained to form a macrocyclic ring. Such a bidentate-chelate complex is possible only if the coordination takes place through the 1,4-positions of the hexatomic piperazine ring with two aliphatic chain and a terminal amino[3,4] group ($R_2N—CH_2—CH_2—NH_2$)

The substituted piperazine favours 2:2 condensation[5] yielding a good building block to form large receptor molecules.[6]

The edge that piperazine has over other diamines is its ability to bind metal ions in monodentate[7] (I), bidentate[8] (II) or bridging ligand modes[9] (III). Piperazine-bridged metal complexes were, therefore, synthesised to study and ascertain the mode of linkage of the dithiocarbamato-moiety with transition metal ions.

Experimental

Hydrated metal chlorides (BDH), sodium diethyldithiocarbamate, piperazine (CDH), carbon disulfide, sodium hydroxide (Merck) were used as received. Methanol was used after distillation. Elemental analyses (C, H, N and S) were carried out with a Flash EA1112 Analyser, CE Instrument. IR spectra (4000–350 cm^{-1}) were recorded on a FT IR, Perkin-Elmer Spectrum BX as KBr discs. The conductivity measurements were carried out with a CM-82T Elico conductivity bridge in DMSO. The electronic spectra were recorded on a Cintra 5GBC spectrophotometer in DMSO. Magnetic susceptibility measurements were done with a Sherwood Scientific MSB Auto at room temperature. TGA/DSC was performed with a Universal V3.8 B TA SDT Q600 Build 51 Thermal Analyzer. The experiment was done under a dinitrogen atmosphere using alumina powder as reference material and the heating rate was kept at 20 °C/min and the metal contents were estimated by complexometric titration.[10]

Synthesis of piperazinebisdithiocarbamate (ppzdtc)

The sodium salt of piperazine bisdithiocarbamate (Na_2ppzdtc) was prepared by a literature method.[11] In 150 ml ethanolic solution of piperazine hexahydrate (50 mmol, 9.71 g) kept below 0 °C, was added neat carbon disulfide (100 mmol, 6.04 ml) dropwise over 1 h to obtain an instantaneous white precipitate. To this reaction mixture NaOH (100 mmol, 4.0 g), dissolved in minimum amount of double distilled water, was added and the stirring was continued for an additional four hours. The mixture was left overnight to yield a white crystalline product. It was filtered, washed several times with ethanol and ether and dried *in vacuo* over $CaCl_2$.

Synthesis of complexes

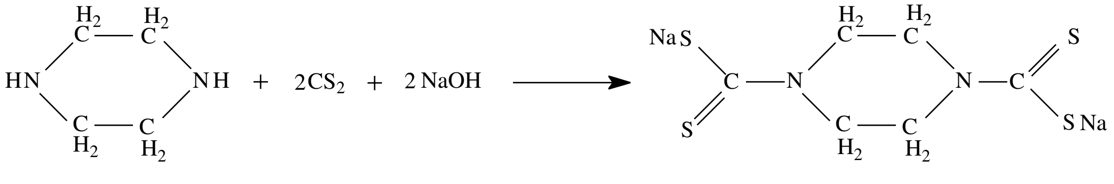
To an ethanolic solution (25 ml) of hydrated metal(II) chloride (2 mmol) was added ethanolic solutions (20 ml) of sodium diethyldithiocarbamate (2 mmol, 0.45 g) and sodium piperazine bisdithiocarbamate (1 mmol, 0.28 g) simultaneously with vigorous stirring to obtain an immediate precipitation of the respective metal complex. The reaction mixture was refluxed for about 5 h until it afforded complete precipitation. It was then cooled, the solid product was filtered and washed repeatedly with methanol and ether and dried *in vacuo*.

Results and discussion

The complexes are thermally stable and decompose between 150 and 288 °C. They are soluble in DMSO and DMF. The result of elemental analyses (Table 1) correspond to the composition [{M(etdtc)}$_2$ppzdtc] and [{M^1(etdtc)$_2$}$_2$ppzdtc] (where M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II), M^1 = Cr(III), Fe(III), etdtc = ($S_2NC_5H_{10}$) and ppzdtc = [$S_2C(NCH_2CH_2)_2CS_2$]). The molar conductance of 1 mmol solutions of the complexes measured in DMSO indicated that they are non-electrolytes.[12]

IR spectra (Table 2)

The skeletal vibrational modes of the piperazine in all the complexes are slightly shifted towards lower frequencies suggesting a distortion of the chair conformation[13,14] upon coordination. The ν(C–S) value



Scheme 1 Formation of ligand Na_2ppzdtc

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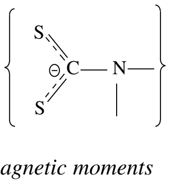
Table 1 Analytical data and physical properties of the complexes

Compounds (F.W)	Colour	M. p./°C	Yield/%	Molar conductance ($ohm^{-1}mol^{-1}cm^2$)	Analysis, (%) Found (calcd).				
					C	H	N	S	M
Na_2ppzdtc	White	110	81	41.1	25.7	2.6	9.8	45.7	–
(282.4)					(25.5)	(2.9)	(9.9)	(45.4)	
[{Mn(etdtc)}$_2$ppzdtc]	Light brown	140	55	13.1	29.7	4.6	8.6	39.8	16.8
(618.7)					(29.9)	(4.4)	(8.7)	(39.9)	(17.1)
[{Fe(etdtc)}$_2$ppzdtc]	Dark brown	260	62	32.5	29.7	4.6	8.5	39.6	17.0
(620.6)					(29.8)	(4.4)	(8.7)	(39.8)	(17.3)
[{Co(etdtc)}$_2$ppzdtc]	Green	180	67	17.2	29.4	4.4	8.6	39.3	17.9
(626.7)					(29.5)	(4.3)	(8.6)	(39.4)	(18.1)
[{Ni(etdtc)}$_2$ppzdtc]	Algae green	225	70	31.7	29.4	4.9	8.5	39.3	18.2
(626.3)					(29.6)	(4.3)	(8.6)	(39.4)	(18.1)
[{Cu(etdtc)}$_2$ppzdtc]	Yellow	288	68	10.8	28.9	4.4	8.4	38.7	19.1
(635.9)					(29.1)	(4.3)	(8.5)	(38.9)	(19.3)
[{Zn(etdtc)}$_2$ppzdtc]	Yellow	105	55	8.7	28.7	4.5	8.1	38.5	19.5
(639.6)					(29.0)	(4.3)	(8.4)	(38.7)	(19.7)
[{Cd(etdtc)}$_2$ppzdtc]	Dirty white	118	48	9.2	25.7	3.5	7.2	33.7	29.4
(733.68)					(25.4)	(3.7)	(7.4)	(33.9)	(29.7)
[{Hg(etdtc)}$_2$ppzdtc]	Black	210	72	14.7	20.8	3.4	5.7	27.2	42.6
(910.1)					(20.6)	(3.0)	(6.0)	(27.5)	(43.0)
[{Cr(etdtc)$_2$}$_2$ppzdtc]	Blue-green	110	70	21.6	32.4	4.6	9.4	43.7	9.0
(933.4)					(32.9)	(4.8)	(9.6)	(43.9)	(8.9)
[{Fe(etdtc)$_2$}$_2$ppzdtc]	Dark brown	140	70	41.1	33.2	5.2	9.1	40.7	11.5
(941.1)					(33.2)	(5.1)	(8.9)	(40.9)	(11.9)

Table 2 Cardinal IR stretching frequencies and their assignments

Compounds	ν(M–S)	ν(C–S)	ν(C–N)	ν(N–H)	Skeletal vibrations
Piperazine	–	–	–	3266 m	1300 w
[{Mn(etdtc)}$_2$ppzdtc]	498	997 s	1495 m	–	1273 m
[{Fe(etdtc)}$_2$ppzdtc]	496	997 s	1495 m	–	1272 m
[{Co(etdtc)}$_2$ppzdtc]	486	998 s	1494 m	–	1274 m
[{Ni(etdtc)}$_2$ppzdtc]	490	996 s	1497 m	–	1277 m
[{Cu(etdtc)}$_2$ppzdtc]	488	996 s	1495 m	–	1267 m
[{Zn(etdtc)}$_2$ppzdtc]	485	994 s	1495 m	–	1272 m
[{Cd(etdtc)}$_2$ppzdtc]	492	998 s	1496 m	–	1273 m
[{Hg(etdtc)}$_2$ppzdtc]	479	993 s	1495 m	–	1272 m
[{Cr(etdtc)$_2$}$_2$ppzdtc]	488	998 s	1496 m	–	1274 m
[{Fe(etdtc)$_2$}$_2$ppzdtc]	484	996 s	1495 m	–	1271 m

is very diagnostic of the nature of bonding of the dithiocarbamates. The region 1070–930 cm^{-1} has been found to be indicative of ν(C–S).[15] It has been observed in a variety of dithiocarbamato-complexes and it is certain that appearance of a single sharp band around 1000±70 cm^{-1} is due to the bidentate coordination while splitting of this band within a narrow range of 20 cm^{-1} is due to the monodentate nature of the dithiocarbamato-group.[16] In the present study, we observed only a single sharp band, at 1000±10 cm^{-1} in all the complexes indicating bidentate bonding of the dithiocarbamato-group. A thioureide band near 1500 cm^{-1} is a characteristic feature of dithiocarbamates and indicates partial double bond character in the $S_2C \cdots\cdots NR_2$ bond due to delocalisation of electrons. The ν(C ⋯⋯ N) value seems to be insensitive to the nature of the metal.[16] We have observed a strong band at 1495 cm^{-1} which is intermediate between ν(C–N) and ν(C=N) indicating a partial double bond character. However, there are two factors[17] which effect the M–S peak position occurring in the far-IR region: (i) the nature of the metal ion and (ii) the substituents attached to the nitrogen. In the present study some weak intensity bands are observed in the 500 cm^{-1} range corresponding to the ν(M–S) values in agreement with other authors.[18]



Electronic spectra and magnetic moments

The electronic spectral bands and the magnetic moments of the complexes are listed in Table 3. All the known octahedral Cr(III) complexes have been found to have three unpaired electrons irrespective of the field strength of the ligands. The magnetic moment value of such complexes lies around 3.88 B.M. In the present case a value of 3.74 B.M. was obtained for the green [{Cr(etdtc)$_2$}$_2$ppzdtc]. The electronic spectra of the complexes in DMSO exhibit bands at 15,527; 21,052 and 26,385 cm^{-1} corresponding to $^4T_{2g}$ (F) ← $^4A_{2g}$ (F); $^4T_{1g}$ (F) ← $^4A_{2g}$ (F) and $^4T_{1g}$ (P) ← $^4A_{2g}$ (F) transitions, respectively, further supporting an octahedral environment around Cr(III) ion.[19]

In the complex [{Fe(etdtc)$_2$}$_2$ppzdtc], Fe(III) is surrounded by six sulfur donors[20] similar to octahedral [Fe(diethyldithiocarbamate)$_3$]. The magnetic moment value of 2.53 B.M. is too low to suggest a spin free Fe(III) but it appears to be intermediate between high-spin (5.9 B.M.) and low-spin (2.3 B.M.), suggesting a high-spin – low-spin cross over.[21] The characteristic feature of Fe(III)-dithiocarbamates is the presence of intense absorption bands due to both M → L and L → M charge transfer.[22] We have observed three bands at 17,241; 19,880 and 26,041 cm^{-1} corresponding to $^4T_{1g}$(G) ← $^6A_{1g}$; $^4T_{2g}$(G) ← $^6A_{1g}$ and ^4E_g ← $^6A_{1g}$ transitions, respectively. A sharp charge transfer shoulder at 29,411 cm^{-1} has also been observed which is commonly found in octahedral Fe(III) dithiocarbamato-complexes.[21]

Unlike octahedral Fe(III) complexes, the tetrahedral high-spin Fe(II) complex shows only one spin allowed d-d absorption at 20,022 cm^{-1} corresponding to the ^5E ← $^5T_2$ transition. The magnetic moment value of tetrahedral Fe(II) complexes lies between 5.0-5.5 B.M. corresponding to four unpaired electrons. The value in the present investigation is 5.05 B.M. which is consistent with the tetrahedral nature of Fe(II) in [{Fe(etdtc)}$_2$ppzdtc].[23]

Generally, the tetrahedral Mn(II) complexes are high-spin and exhibit spin forbidden transitions. The pale yellow complex shows an intense absorption band in the visible region at 17,513 cm^{-1} assigned to the $^4T_1$ ← $^6A_1$ transition. In addition, it also shows a strong charge transfer band at 33,851 cm^{-1}. The magnetic moment of 5.77 B.M. of

Table 3 Magnetic moment values and spectral bands of the complexes

Compounds	Magnetic moment (B.M.)	Electronic bands/cm^{-1}	log ε (l mol^{-1} cm^{-1})	Possible assignments	10 Dq/cm^{-1}	B/cm^{-1}	β
[{Cr(etdtc)$_2$}$_2$ppzdtc]	3.74	26,385 21,052 15,527	2.57 2.49 2.42	$^4T_{1g}$ (P) ← $^4A_{2g}$ (F) $^4T_{1g}$ (F) ← $^4A_{2g}$ (F) $^4T_{2g}$ (F) ← $^4A_{2g}$ (F)	15,760	477	0.58
[{Fe(etdtc)$_2$}$_2$ppzdtc]	2.53	26,041 19,880 17,241	3.94 3.56 3.46	^4E_g (D) ← $^6A_{1g}$ $^4T_{2g}$(G) ← $^6A_{1g}$ $^4T_{1g}$ (G) ← $^6A_{1g}$	17,750	412	0.89
[{Mn(etdtc)}$_2$ppzdtc]	5.77	33,851 17,513	2.39 1.52	Charge transfer $^4T_1$ ← $^6A_1$	–	–	–
[{Fe(etdtc)}$_2$ppzdtc]	5.05	31,250 26,246 20,022	3.58 3.10 2.78	Charge transfer Charge transfer ^5E ← $^5T_2$	–	–	–
[{Co(etdtc)}$_2$ppzdtc]	4.38	27,845 17,513 16,025	3.55 3.02 3.05	Charge transfer $^4T_1$ (F) ← $^4A_2$ (F) $^4T_2$ (F) ← $^4A_2$ (F)	16,120	463	0.90
[{Ni(etdtc)}$_2$ppzdtc]	Diamagnetic	22,883 15,898	2.69 2.19	$^1B_{1g}$ ← $^1A_{1g}$ $^1A_{2g}$ ← $^1A_{1g}$	15,960	–	–
[{Cu(etdtc)}$_2$ppzdtc]	1.76	22,371 15,479	2.70 2.42	$^2B_2$g ← $^2B_1$g $^2A_1$g ← $^2B_1$g	–	–	–

Mn(II) in [{Mn(etdtc)}$_2$ppzdtc] is near the calculated spin-only value of 5.9 B.M. indicating a tetrahedral arrangement of the Mn(II) ion.[19]

Tetrahedral or pseudo-tetrahedral d^7 high-spin Co(II) complexes are generally deep blue and exhibit three electronic spectral bands.[19] Two of the three bands appear in the IR region while the third one appears in the red region between 13,000 and 18,000 cm^{-1}. The absorptions at 16,025 cm^{-1} and 17,513 cm^{-1} observed in this work may be attributed to $^4T_2$(F) ← $^4A_2$(F) and $^4T_1$(F) ← $^4A_2$(F) transitions, respectively. However, Marcotrigiano *et al.*[24] found these two bands at 15,000 and 16,950 cm^{-1}. The magnetic moment value of 4.38 B.M. further establishes the tetrahedral geometry for [{Co(etdtc)}$_2$ppzdtc] complex.

The green solution of [{Ni(etdtc)}$_2$ppzdtc] in DMSO shows two sharp bands at 15,898 and 22,883 cm^{-1} corresponding to $^1A_{2g}$ ←$^1A_{1g}$ and $^1B_{1g}$ ←$^1A_{1g}$ transitions, respectively, in addition to a shoulder at 21,141 cm^{-1}. Since it is diamagnetic a square-planar[25] geometry for the Ni(II) ion is ascertained.

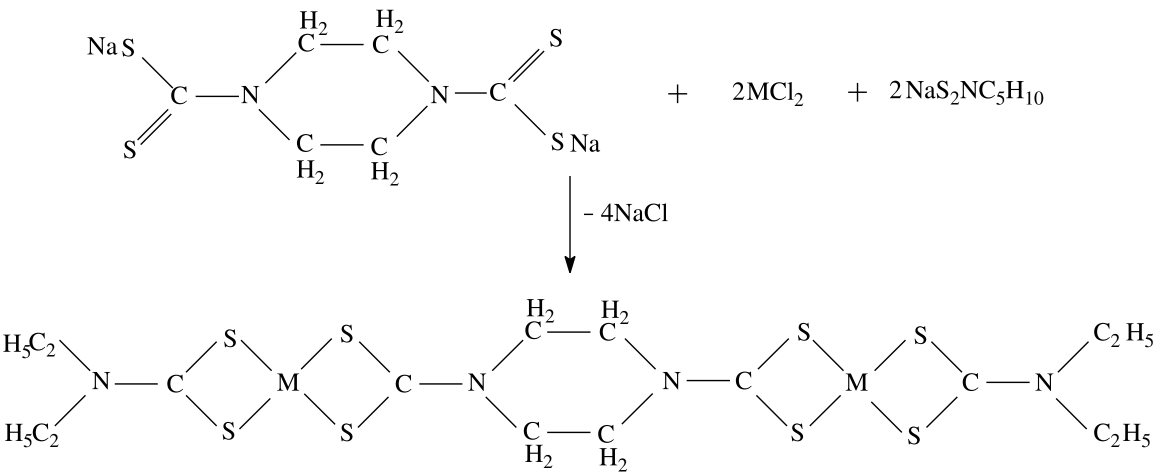
The electronic spectrum of [{Cu(etdtc)}$_2$ppzdtc] shows two bands at 15,479 and 22,371 cm^{-1} assigned to ^2E_g ← $^2B_{1g}$ and $^2A1_{1g}$ ← $^2B1_{1g}$ transitions, respectively, and is interpreted in terms of square-planar geometry.[26] The absence of any band below 10,000 cm^{-1} rules out the possibility of a tetrahedral or pseudo-tetrahedral environment in the complex.[27] The magnetic moment (1.76 B.M.) for Cu(II) ion corresponds to one unpaired electron as has also been found for the Cu(II) ion in square-planar [Cu(dimethylglyoxime)$_2$].[23]

^1H NMR

In the compound [{Cu(etdtc)}$_2$ppzdtc], a triplet was observed at 0.79 ppm for the methyl protons of diethyldithiocarbmato-groups, whereas the methylene protons were found to resonate at 3.73 ppm as multiplet.[28] Another singlet at 3.45 ppm was also observed corresponding to eight protons of the piperazine moiety, thus confirming the proposed structure of the compound (Scheme 2).

TGA/DSC

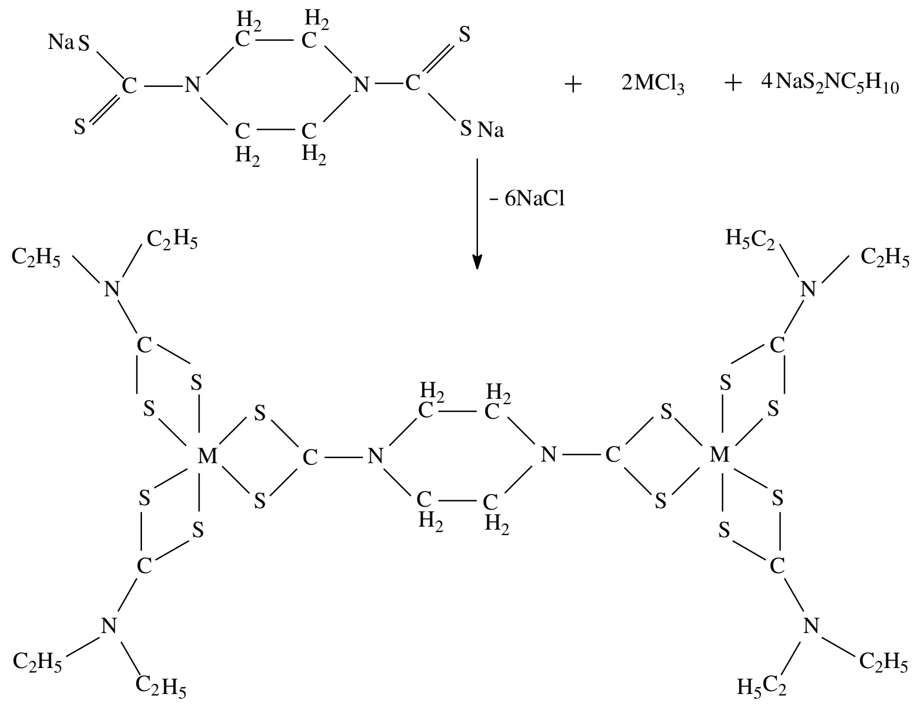
Generally the dithiocarbamato-complexes either volatilise, leaving some residues or decompose to the corresponding metal sulfide.[29] However, the mixed ligand diethyldithiocarbamates with a variety of chelating ligands are found to be non-volatile[22] and the alkyl substituents on the dithiocarbamato core do not influence the decomposition process. In the present work the sample was heated at the rate of 20 °C/min under a dinitrogen atmosphere. A simple two step decomposition was observed as has been found by D'Ascenzo and Wendlendt in the case of Fe(III) diethyldithiocarbamates.[30] The thermograms do not show any change until 175 °C, discarding the possibility of any coordinated water or solvent molecule. The first step of pyrolysis (Table 4) ranges from 200–390 °C, corresponding to the decomposition of the whole organic moiety. The total weight loss of about 60–70 % is observed and the decomposition step appears to be a slower one. The second stage of pyrolysis occurs at 400–600 °C. The weight loss data for this step correspond to the formation of the appropriate metal sulfide as the final product. Criado et al[31] reported a multistep decomposition for Pt(II) dithiocarbamates derived from



Scheme 2 Preparation of [{M(etdtc)}$_2$ppzdtc] where M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II); etdtc = $S_2CN(C_2H_5)_2$ and ppzdtc = $[S_2C(NCH_2CH_2)_2CS_2]$.

Table 4 Degradation of various fragments in the complexes

Complexes	First decomposition stage			Second decomposition stage		
	Fragments	Temperature range/°C	Mass loss data, found (calcd.) %	Fragments metal sulfide	Temperature range/°C	Mass loss data, found (calcd.) %
[{Mn(etdtc)}$_2$ppzdtc]	Whole organic moiety	209–344	60.88 (61.51)	2MnS$_2$	400–600	38.10 (38.48)
[{Fe(etdtc)}$_2$ppzdtc]	–do-	175–325	65.81 (66.50)	Fe$_2$S$_3$	–do-	32.87 (33.49)
[{Co(etdtc)}$_2$ppzdtc]	–do-	175–325	70.52 (70.96)	2CoS	–do-	28.74 (29.04)
[{Ni(etdtc)}$_2$ppzdtc]	–do-	224–390	72.31 (71.01)	2NiS	–do-	27.56 (28.98)
[{Cu(etdtc)}$_2$ppzdtc]	–do-	225–325	69.12 (69.93)	2CuS	–do-	30.51 (30.06)
[{Zn(etdtc)}$_2$ppzdtc]	–do-	220–375	68.29 (69.53)	2ZnS	–do-	31.11 (30.47)



Scheme 3 Preparation of [{M(etdtc)$_2$}$_2$ppzdtc] where M = Cr(III) and Fe(III) etdtc = $S_2CN(C_2H_5)_5$ and ppzdtc = $[S_2C(NCH_2CH_2)_2CS_2]$.

α-amino acids. They showed the formation of metallic platinum while some workers[32] have reported the formation of Pt-sulfide from Pt(II)-dithiocarbamates. The final product in our case is always metal sulfide.

The DSC curves also correlate well with the TGA data. A broad endothermic band is observed from 75 to 125 °C in all the TGA profiles, implying a phase change of the complex prior to any decomposition and no weight loss step. A second broad exothermic band is observed at around 350 °C, establishing that the decomposition of the whole organic moiety is an exothermic process. However, there is no distinct peak corresponding to the final step for the formation of metal sulfide.

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