

A HETEROTRIMETALLIC CHAIN CONSTRUCTED FROM BINUCLEAR [Cu(II)Mn(II)] NODES AND *trans*-[Cr(NCS)₄(pyz)₂]⁻ SPACERS

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The assembly process between [LCuMn]²⁺ cations and *trans*-[Cr(NCS)₄(pyz)₂]⁻ anions affords a linear heterotrimetallic cationic chain, [$\{\text{LCuMn}(\text{H}_2\text{O})\}\{\text{Cr}(\text{NCS})_4(\text{pyz})_2\}_n$]ⁿ⁺, whose charge is counterbalanced by [Cr(NCS)₄(pyz)₂]⁻ ions [(H₂L = the dissymmetric compartmental Schiff-base proligand resulted from the condensation of 2,6-diformyl-4-methyl-phenol with ethylenediamine and diethylenetriamine; pyz = pyrazine).

INTRODUCTION

The search for rational synthetic routes leading to heterometallic complexes is of current interest in molecular magnetism.¹ The combination of different spin carriers within the same molecular entity leads to interesting magnetic and spectroscopic properties. While heterobimetallic complexes are quite common, the number of coordination compounds containing three different metal ions, all of them paramagnetic, is still limited to only few examples. Most of these are 3d-3d'-3d'' or 3d-3d'-4f systems, and are either discrete species, or coordination polymers with various dimensionalities.²

The very first discrete complexes with three different 3d metal ions have been synthesized by Chaudhuri *et al.*³ Their synthetic strategy is based upon the use of unsymmetrical bicompartamental Schiff-base oxime ligands, which encapsulate two different metal ions, M_B and M_C. The preformed bimetallic oximate can further act as a ligand towards the third metal ion, M_A, whose coordination sphere is partially blocked by a capping ligand, tmtacn (1,4,7-trimethyl-1,4,7-triazacyclononane). An alternative way in designing heterotrimetallic complexes consists of self-assembly processes between heterobimetallic

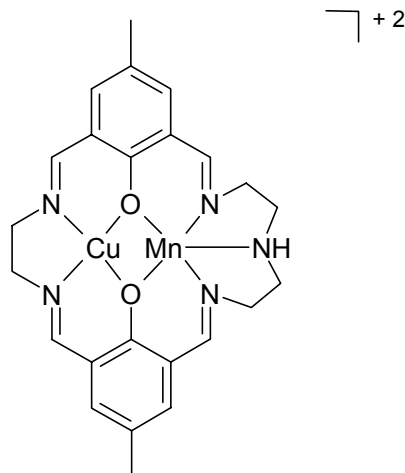
cations and anionic complexes with potentially bridging ligands (*e. g.* cyanido or oxalato ions).⁴ Following this synthetic approach we obtained 3d-3d'-3d'',⁵ and 3d-3d'-4f complexes.⁶

Interesting metalloligands are the isothiocyanato complexes, for example Reinecke, *trans*-[Cr(NCS)₄(NH₃)₂],⁷ or Reinecke-type complexes, *trans*-[Cr(NCS)₄L₂]⁻. The last ones can be more attractive when the L molecules are *exo*-dentate ligands, that is, organic molecules (pyrazine, 4,4'-bipyridine) which can connect the chromium(III) ion with a second metal ion. Moreover, such species could act as ligands towards the second metal ion either through the sulphur atom, or through the nitrogen atom arising from the L molecule (pyz or 4,4'-bipy). We have recently synthesized a heterobimetallic coordination polymer obtained by connecting binuclear nickel(II) nodes with *trans*-[Cr(NCS)₄(4,4'-bipy)₂]⁻ spacers.⁸ The complex anion coordinates to the nickel atoms through the 4,4'-bipy ligands. This result prompted us to use heterobimetallic nodes, in order to obtain heterotrimetallic complexes. Herein we report the synthesis and the crystal structure of a novel coordination polymer, containing Cu(II), Mn(II) and Cr(III) ions: [$\{\text{LCuMn}(\text{H}_2\text{O})\}\{\text{Cr}(\text{NCS})_4(\text{pyz})_2\}_n$][Cr(NCS)₄(pyz)₂]⁻ **1** (H₂L = the

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dissymmetric compartmental Schiff-base proligand resulted from the condensation of 2,6-diformyl-4-

methyl-phenol with ethylenediamine and diethylenetriamine).



Scheme 1.

EXPERIMENTAL PART

All solvents and chemicals were of analytical grade and have been used as received. 2,6-Diformyl-4-methyl-phenol and the $[N,N'$ -bis(3-formyl-5-methylsalicylidene)ethylenediaminato]copper(II) were prepared according to literature.^{9,10} The binuclear precursor, $[LCuMn](ClO_4)_2 \cdot H_2O \cdot CH_3OH$, has been synthesized following the procedure reported by Okawa *et al.*¹¹ The chromium complex, $trans\text{-}K[Cr(NCS)_4(pyraz)_2]$, has been obtained by refluxing a *i*PrOH solution of $K_3[Cr(NCS)_6]$ and pyrazine (in a 1:2.5 ratio) for 6 h, and isolation of the red solid that appeared on cooling.

The heterotrimeric complex, $\{LCuMn(H_2O)\}[Cr(NCS)_4(pyraz)_2]\} \mathbf{1}$, has been obtained by reacting the binuclear precursor, $[LCuMn]$

$(ClO_4)_2 \cdot H_2O \cdot CH_3OH$ (in MeOH/water solution), with $trans\text{-}K[Cr(NCS)_4(pyraz)_2]$ (in MeOH) in a 1:2 ratio. The slow evaporation of the resulted solution yielded red-violet crystals of the compound **1**, which were filtered, washed with water and dried. In spite of our efforts, we were not able to obtain better quality crystals.

X-ray diffraction measurements were performed at 150K with a Nonius Kappa diffractometer, using graphite monochromated Mo $K\alpha$ radiation. Crystal data, data collection parameters and structure refinement details are given in Table 1. The structure was solved by direct methods and refined by full-matrix least-squares techniques based on F^2 . Calculations were performed using the SHELX-97 crystallographic software package.

Table 1

Crystallographic data and structure refinement parameters for compound **1**

Empirical formula	$C_{48}H_{45}CuMnCr_2N_{21}O_3S_8$
M	1443.01
Temperature [K]	150(2)
Wavelength [\AA]	0.71073
Crystal system	monoclinic
Space group	Cc
a [\AA]	24.259(3)
b [\AA]	15.869(2)
c [\AA]	18.444(3)
β [$^\circ$]	113.105(9)
V [\AA^3]	6530.8(16)
Z	4
ρ (calcd) [Mgm^{-3}]	1.468
μ Mo [mm^{-1}]	1.146
$F(000)$	2936
Gof (for F^2)	1.031
Final R , wR [$I > 2\sigma(I)$]	0.1142, 0.2724
$\Delta\rho_{\text{max}}$ and $\Delta\rho_{\text{min}}$ [$\text{e}\text{\AA}^{-3}$]	0.878 and -0.574

RESULTS AND DISCUSSION

In order to obtain a heterotrimetallic complex, we applied the following stepwise procedure: (1) synthesis of the mononuclear complex [LCu]; (2) synthesis of the binuclear complex, [LCuMn]²⁺; (3) self-assembly process involving the binuclear [LCuMn]²⁺ species and the metalloligand, [Cr(NCS)₄(pyz)₂]. The first two metal ions, Cu(II) and Mn(II), are held together by a dissymmetric compartmental ligand (Scheme 1). The third paramagnetic metal ion, Cr(III), arises from the Reinecke type metalloligand, [Cr(NCS)₄(pyz)₂]. This complex has been obtained by reacting K₃[Cr(NCS)₆] with pyrazine. The infrared spectrum of K[Cr(NCS)₄(pyz)₂] (Fig. 1) clearly shows the presence of the characteristic bands of the two ligands (NCS⁻ and pyz). The ν_{NCS} band in K₃[Cr(NCS)₆] (2092 cm⁻¹) is shifted toward lower frequencies (2078 cm⁻¹) in the Reinecke anion. The characteristic bands of pyrazine in the mixed ligand complex are: $\nu_{\text{C=N}}$: 1417 cm⁻¹, $\delta_{\text{C-H}}$: 1058 cm⁻¹, $\gamma_{\text{C-H}}$: 802 cm⁻¹.

The UV-VIS spectrum of K[Cr(NCS)₄(pyz)₂] exhibits one band at 540 nm, which is assigned to the first d-d transition of Cr(III) in a (pseudo)octahedral environment, ⁴A_{2g} → ⁴T_{2g}. The charge transfer band (with the maximum located at 350 nm) overlaps the two other bands arising from d-d transitions.

The reaction between the binuclear [CuMn] complex and K[Cr(NCS)₄(pyz)₂] leads to [{LCuMn(H₂O)} {Cr(NCS)₄(pyz)₂}][Cr(NCS)₄(pyz)₂] **1**. The single crystal X-ray analysis of **1** reveals

heterotrimetallic cationic chains, [{LCuMn(H₂O)} {Cr(NCS)₄(pyz)₂}]_nⁿ⁺, and [Cr(NCS)₄(pyz)₂] as counterions. In principle, the [Cr(NCS)₄(pyz)₂] ion can act as a ligand towards a second metal ion through the sulphur atom, or through the second pyrazine nitrogen atom. In our case, within the chains, the Reinecke-type anion acts as a spacer, being coordinated to the copper(II) ions from the nodes through the sulphur atoms from two *trans* NCS groups (Fig. 2). The coordination spheres of the metal ions in the trimetallic chain are illustrated in Fig. 3. The copper(II) ions exhibit an elongated octahedral stereochemistry, with the apical positions occupied by the semicoordinated sulphur atoms (Cu1 – S11J = 3.15(1) Å; Cu1 – S11E = 3.24(1) Å). The basal plane is formed by two nitrogen atoms from the Schiff-base ligand, and two phenoxo oxygen atoms, with the Cu – O and Cu – N distances falling in the range 1.86(2) – 2.05(3) Å. The manganese ions are hexacoordinated by two imino nitrogen atoms from the Schiff-base [Mn1 – N10 = 1.88(3); Mn1 – N16 = 2.27(2) Å], one secondary amine nitrogen [Mn1 – N13 = 2.54(2) Å], two phenoxo oxygens [Mn1 – O7 = 2.14(2); Mn1 – O19 = 2.35(2) Å], and one aqua ligand [Mn1 – O1W = 2.35(2) Å]. The intranode Cu(II) ⋯ Mn(II) distance is 3.23(4) Å. The distances between the copper and chromium ions bridged by the NCS ligands are 6.326(8) and 6.344(8) Å. Other relevant bond distances and angles are gathered in Table 2.

Table 2

Selected bond lengths [Å] and angles [°] for compound **1**

Cu(1)–N(1)	2.05(3)	O(7)–Cu(1)–N(1)	166.7(1)
Cu(1)–N(4)	1.88(2)	O(19)–Cu(1)–N(4)	175.4(8)
Cu(1)–O(7)	1.86(2)	N(1)–Cu(1)–N(4)	84.8(8)
Cu(1)–O(19)	1.96(2)	O(7)–Cu(1)–O(19)	85.5(6)
Cu(1)–S(11J)	3.15(1)	S(11J)–Cu(1)–S(11E)	168.7(3)
Cu(1)–S(11E)	3.24(1)	O(1W)–Mn(1)–O(7)	82.2(8)
Mn(1)–N(13)	2.54(2)	O(7)–Mn(1)–O(19)	70.4(5)
Mn(1)–N(10)	1.88(3)	O(19)–Mn(1)–N(16)	74.8(8)
Mn(1)–N(16)	2.27(2)	N(16)–Mn(1)–N(13)	66.8(6)
Mn(1)–O(7)	2.14(2)	N(13)–Mn(1)–N(10)	71.6(7)
Mn(1)–O(19)	2.35(2)	N(10)–Mn(1)–O(1W)	81.4(1)
Mn(1)–O(1W)	2.35(2)	N(10)–Mn(1)–N(16)	114.4(1)
Cr(1)–N(1A)	2.13(2)	N(1B)–Cr(1)–N(11C)	92.1(1)
Cr(1)–N(1B)	2.07(1)	N(1B)–Cr(1)–N(11B)	91.8(1)
Cr(1)–N(11A)	1.97(2)	N(11B)–Cr(1)–N(1A)	80.4(1)
Cr(1)–N(11B)	2.01(4)	N(1A)–Cr(1)–N(11D)	86.4(8)
Cr(1)–N(11C)	1.87(3)	N(1D)–Cr(2)–N(11J)	91.8(9)
Cr(1)–N(11D)	2.13(2)	N(1C)–Cr(2)–N(11J)	84.1(9)
Cr(2)–N(11E)	2.18(3)	N(1D)–Cr(2)–N(11E)	91.0(9)
Cr(2)–N(1D)	2.08(1)	N(1C)–Cr(2)–N(11E)	93.3(9)
Cr(2)–N(11I)	2.06(3)		
Cr(2)–N(11J)	1.83(2)		
Cr(2)–N(1C)	2.12(1)		
Cr(2)–N(11F)	1.86(2)		

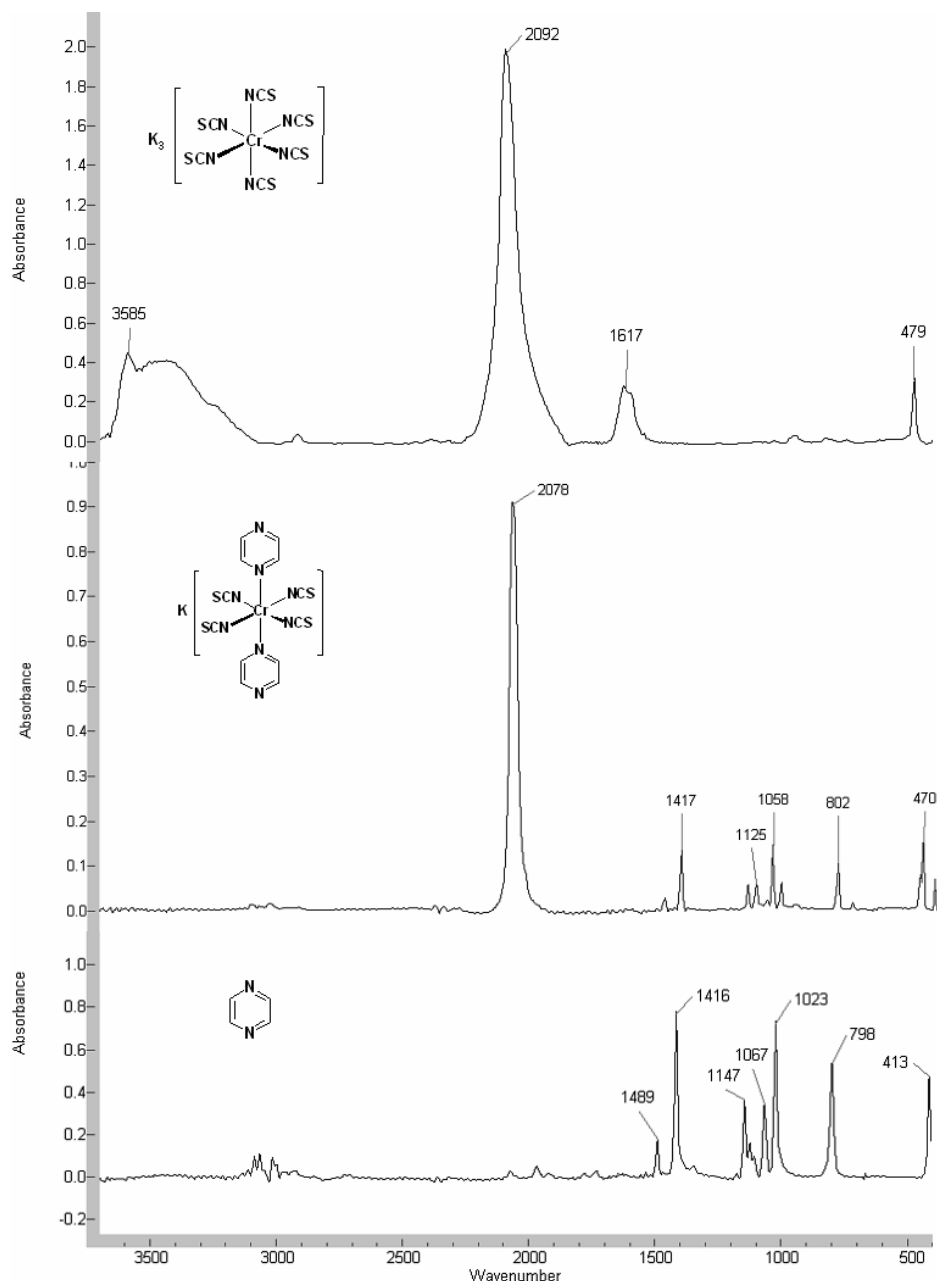


Fig. 1 – Infrared spectra of $K_3[Cr(NCS)_6]$, $trans\text{-}K[Cr(NCS)_4(pyz)_2]$, and pyrazine.

The analysis of the packing diagram reveals interesting interactions at the supramolecular level: (a) sulphur \cdots sulphur contacts (3.97 Å) between the spacers arising from adjacent chains (Fig. 4); (b) $\pi\text{-}\pi$ stacking interactions (3.33 Å) occurring between the pyrazine rings from uncoordinated $[Cr(NCS)_4(pyz)_2]^-$ ions (Fig. 5); (c) T-shape, C-H $\cdots\pi$ interactions (3.50 Å) established between a pyrazine ligand from a coordinated $[Cr(NCS)_4(pyz)_2]^-$ ion and the aromatic ring arising from the Schiff-base ligand (Fig. 6).

The diffuse reflectance electronic spectra of **1** can be viewed a superposition of the UV-VIS

spectra of the two precursors, $[LCuMn](ClO_4)_2\cdot H_2O\cdot CH_3OH$ and $K[Cr(NCS)_4(pyz)_2]$, as illustrated in Fig. 7. The magnetic susceptibility, χ_M , of compound **1** was measured at room temperature. The value of the $\chi_M T$ product (8.31 $cm^3 mol^{-1} K$) corresponds to the one calculated for the uncoupled metal ions (8.50 $cm^3 mol^{-1} K$, assuming $g_{Cu} = g_{Mn} = g_{Cr} = 2.00$).

In conclusion, we have illustrated with a new example that the self-assembly process involving binuclear heterometallic tectons and metalloligands represents a successful strategy for obtaining heterotrimetallic complexes.

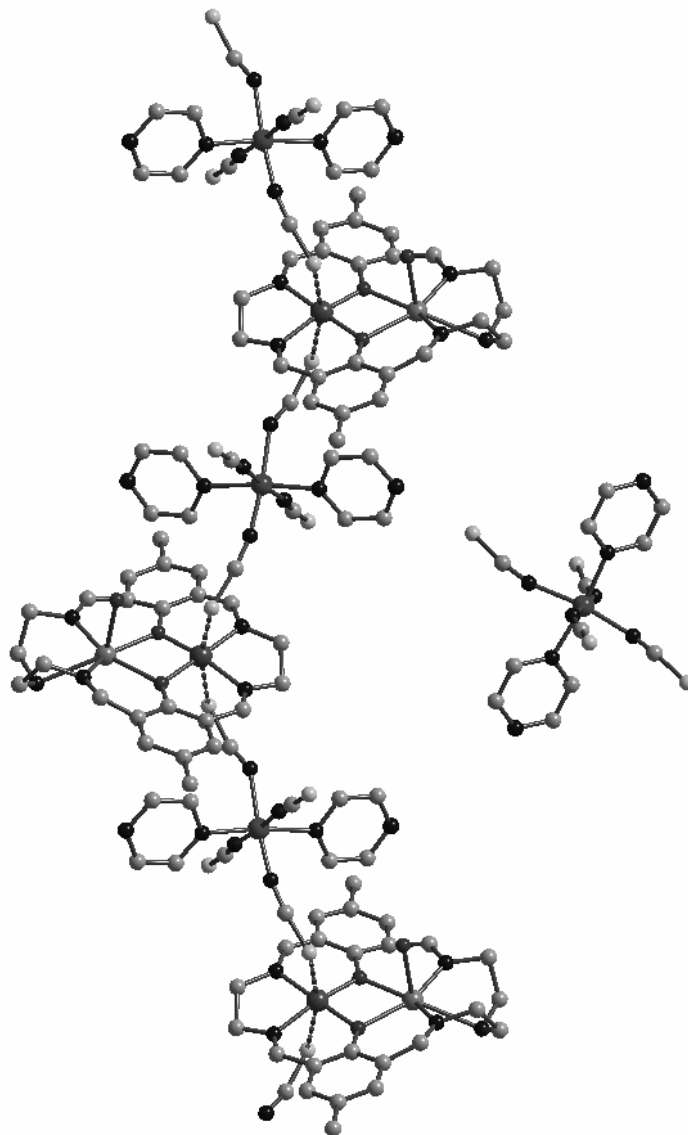


Fig. 2 – Perspective view of the cationic chain and of the uncoordinated $[\text{Cr}(\text{NCS})_4(\text{py})_2]^+$ ion in crystal **1**.

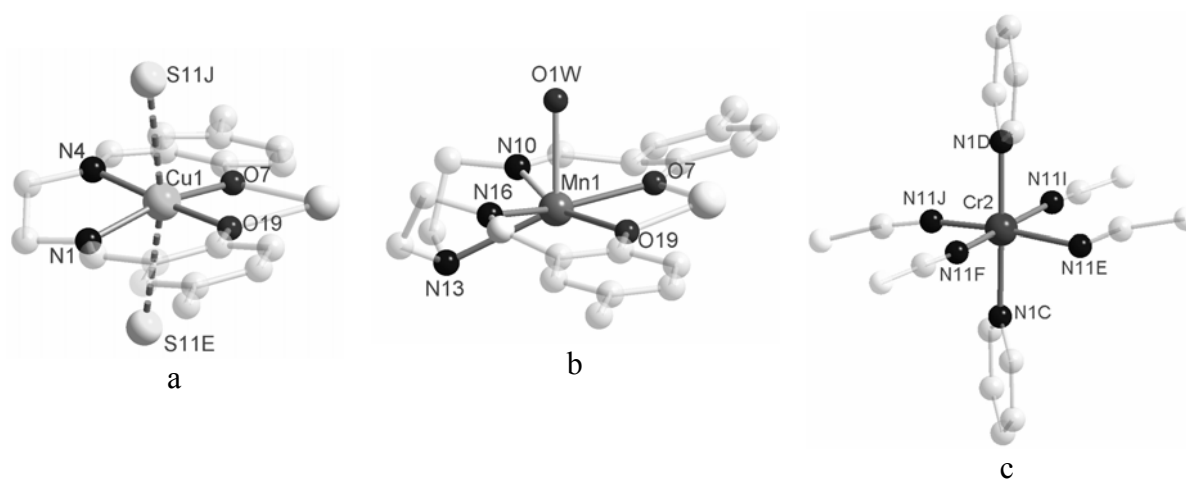


Fig. 3 – Coordination environments of the metal ions in the heterotrimetallic chain.

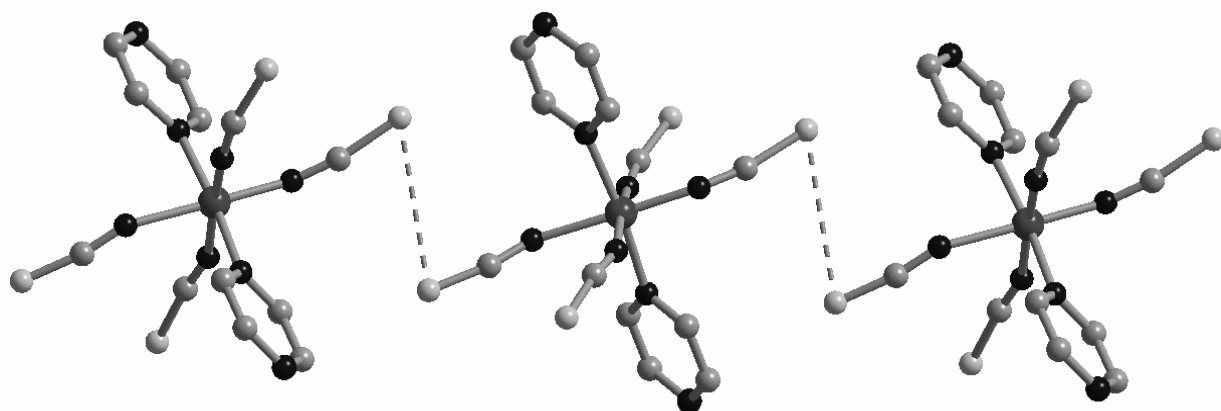


Fig. 4 – Sulphur...sulphur interactions between the coordinated $[\text{Cr}(\text{NCS})_4(\text{pyz})_2]^-$ ions.

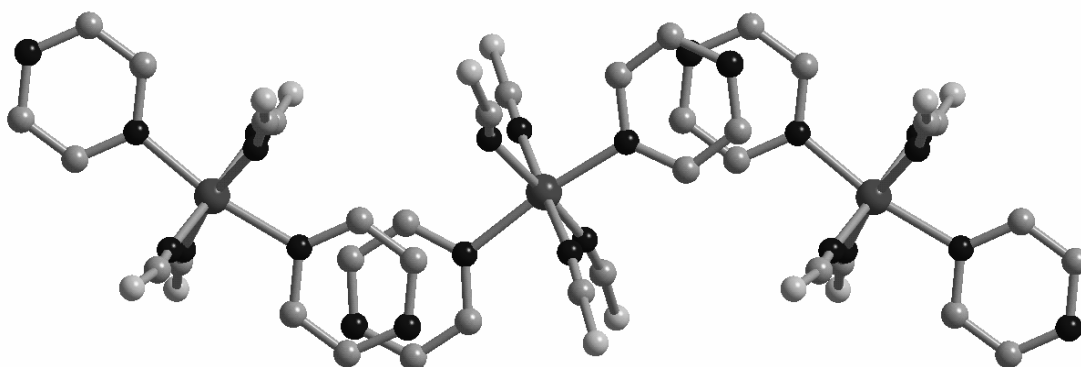


Fig. 5 – π - π Stacking interactions between the uncoordinated $[\text{Cr}(\text{NCS})_4(\text{pyz})_2]^-$ ion.

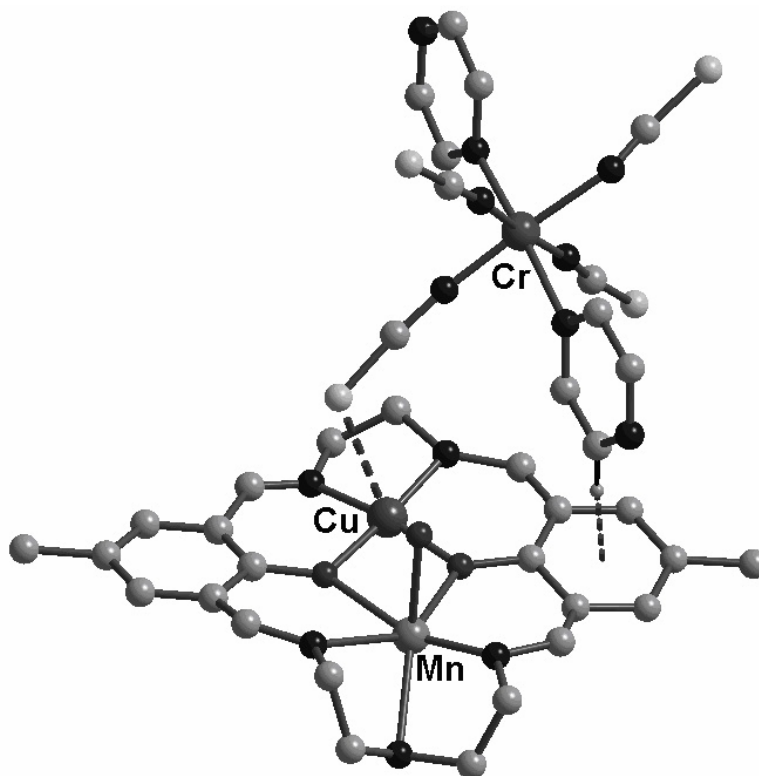


Fig. 6 – C-H... π interactions established between a pyrazine ligand from a coordinated $[\text{Cr}(\text{NCS})_4(\text{pyz})_2]^-$ ion and the aromatic ring arising from the Schiff-base ligand.

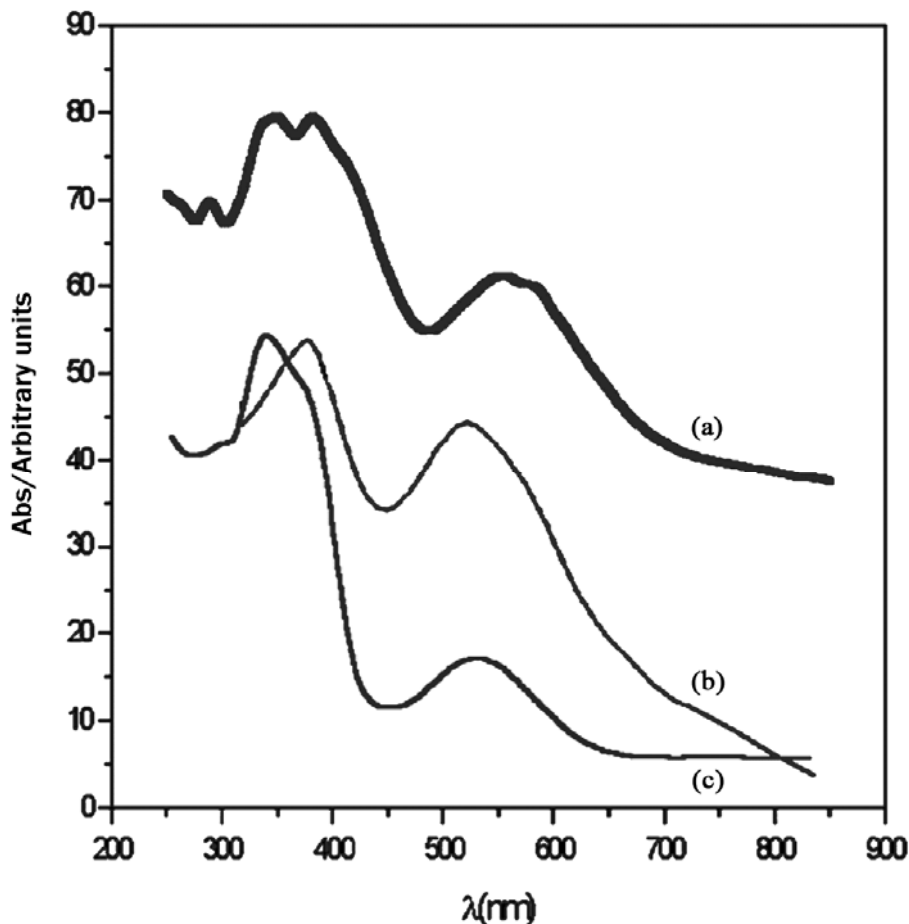


Fig. 7 – The diffuse reflectance electronic spectra of **1** (a); $[\text{LCuMn}](\text{ClO}_4)_2 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{OH}$ (b) and $\text{K}[\text{Cr}(\text{NCS})_4(\text{pyz})_2]$ (c).

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