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Copper(I) pseudohalide complexes with 4,6-dimethylpyrimidine-2(1H)-thione and triphenylphosphane as ligands. The X-ray crystal structures of $[Cu(N_3)(dmpymtH)(PPh_3)_2]$ and $[Cu(NCS)(dmpymtH)(PPh_3)_2]$ ☆

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Abstract

The preparation of mixed-ligand copper(I) coordination compounds containing pseudohalides (azide and thiocyanate), 4,6-dimethylpyrimidine-2(1H)-thione (dmpymtH), and triphenylphosphane is described. The crystalline and molecular structure of $[Cu(N_3)(dmpymtH)(PPh_3)_2]$ (**2**) and $[Cu(NCS)(dmpymtH)(PPh_3)_2]$ (**3**) have been determined by X-ray diffraction methods. The copper atom has a tetra-coordinate $CuNP_2S$ chromophore with distorted tetrahedral coordination in both complexes. Vibrational and ^1H, ^{13}C, ^{31}P NMR spectra of the complexes are discussed and related to the structures. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Synthesis; Copper(I) complexes; Pseudohalides; Crystal structures; Dimethylpyrimidinethione; NMR spectroscopy

1. Introduction

Heterocyclic thiones have attracted considerable attention because of their relevance in biological systems. Sulphur-containing pyrimidine nucleotides have been isolated from hydrolysates of *Escherichia coli* transfer RNA [1]. Recently, the versatility of their coordination forms has been demonstrated in a number of complexes, yielding a variety of coordination compounds with great structural diversity: neutral S-monodentate [2–7]; anion S-monodentate [8,9]; N,S-chelate [8,10–15]; neutral μ_2-S-bridge [16]; anion μ_2-S- [10,17]; μ_2-(S,N)- [18–20]; μ_3-(S,N)- [14,21,22]; μ_4-(S,N)-bridge [21,22]. The copper(I) clusters of the type $[Cu(L)]_n$ ($n = 4$; L = 1-methyl-1,3-imidazoline-2-thiolato [23], $n = 6$; L = 4,6-dimethylpyrimidine-2-thiolato [24]) have been structurally characterised. Mixed-ligand copper complexes of the general formula $[CuX(PPh_3)_nL]$ (X = halide; L = heterocyclic thione) have recently been reported [6,7]. In this paper we report the synthesis and structural characterisation of neutral mononuclear copper(I) pseudohalide (N_3^- and NCS^-) complexes containing 4,6-dimethylpyrimidine-2(1H)-thione and triphenylphosphane as ligands.

2. Experimental

2.1. Reagents and apparatus

All reagents and solvents were of reagent grade and were used without further purification. The compound 4,6-dimethylpyrimidine-2(1H)-thione (dmpymtH) [25]

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and the complex [$CuCl(PPh_3)_3$] [26] were prepared according to reported methods. Microanalyses (C, H, and N) were performed in a Carlo Erba 1104 elemental analyser. Copper was analysed by the standard complexometric method [27]. IR spectra of KBr pellets were recorded on a BOMEM Hartmann & Braun MB-FT in the 4000–400 cm^{-1} region. NMR spectra of the $CDCl_3$ solution were recorded using a Bruker AC250, DPX300 or DRX500 spectrometer. All low temperature experiments were carried out with the 500 MHz instrument using a BSV300 low temperature unit. Tetramethylsilane (Me_4Si) was used as chemical shift reference for ^1H and ^{13}C and 85% H_3PO_4 (ext.) for ^{31}P.

2.2. Preparation of copper(I) complexes

*2.2.1. [$Cu(N_3)(PPh_3)_3$] (**1**)*

To a dichloromethane solution (50 ml) containing [$CuCl(PPh_3)_3$] (3.77 g, 4.25 mmol) and triphenylphosphane PPh_3 (1.11g, 4.25 mmol), a methanolic solution (18 ml) containing sodium azide NaN_3 (306 mg, 4.71 mmol) was added. The resultant suspension was magnetically stirred for 6 h. The suspension was filtered under reduced pressure and hexane (15 ml) was added to the filtrate. The solution was kept at − 15°C and the crystals were collected by filtration after a week and washed thoroughly with hexane. Yield 85% (3.3 g). m.p. > 175°C (dec.). *Anal.* Found: C, 72.91; H, 4.75; Cu, 7.06; N, 4.87. Calc. for $C_{54}H_{45}CuN_3P_3$: C, 72.68; H, 4.71; Cu, 7.12; N, 5.08%. NMR (298 K): ^1H (250 MHz) δ 7.63–7.06 ppm (m, Ph); $^{13}C\{^1H\}$ (62.9 MHz) δ 134.5, 134.1, 129.7, 128.8 ppm; $^{31}P\{^1H\}$ (101.2 MHz) δ − 1.87 ppm (s). IR 3050m, 2037 (ν_{assim} N_3)vs, 1963w, 1584w, 1479m, 1434s, 1308w, 1277w, 1266w, 1183w, 1157w, 1092m, 1026w, 998w, 745s, 726m, 695vs, 517s, 504m, and 441w cm^{-1} (IR data: vs, very strong; s, strong; m, medium; w, weak).

*2.2.2. [$Cu(N_3)(dmpymtH)(PPh_3)_2$] (**2**)*

To a suspension of [$Cu(N_3)(PPh_3)_3$] (892.4 mg, 1 mmol) in dichloromethane (20 ml), dmpymtH (140.2 mg, 1 mmol) was added slowly. The yellow suspension was magnetically stirred for 1 h and then filtered under reduced pressure. Hexane (15 ml) was added to the filtrate and it was kept at − 15°C in a stopped flask. After 2 weeks, the yellow crystals were recovered by filtration, washed thoroughly with hexane and dried using a vacuum pump. Yield 330 mg (43%), m.p. > 130 °C (dec.). *Anal.* Found: C, 64.97; H, 4.86; Cu, 8.17; N, 9.09. Calc. for $C_{42}H_{38}CuN_5P_2S$: C, 65.48; H, 4.97; Cu, 8.25; N, 9.09%. NMR (298 K): ^1H (300 MHz) δ 7.42–7.20 (m, C_6H_5, 30H), 6.23 (br, C3–H, 1H) 2.17 (br, CH_3, 6H) ppm; $^{13}C\{^1H\}$ (75.4 MHz) δ 164.07, 134.7, 133.7, 129.2, 128.3 and 22.4 ppm; $^{31}P\{^1H\}$ (121.5 MHz) δ 0.17 (s) and − 2.52 (s) ppm. IR: 3328w, 3053m, 2583–2547w, 2034 (ν_{assim} N_3)vs, 1621s, 1577vs, 1536w, 1479m, 1434s, 1384m, 1320m, 1256m, 1237s, 1196m, 1092m, 1026w, 996w, 986w, 941w, 890w, 825w, 749s, 694s, 524m, 516s, 501m, 473w, 461m and 440w cm^{-1}.

*2.2.3. [$Cu(NCS)(dmpymtH)(PPh_3)_2$] (**3**)*

To an excess of melted PPh_3 (1.31g, 5 mmol), (dmpymtH) (140.2 mg, 1 mmol) was added and magnetically stirred. The compound CuSCN (121.6 mg, 1 mmol) was added when the temperature reached 110°C and it was maintained for 1 h with occasional stirring. After cooling, dichloromethane (12 ml) was added and the suspension filtered under reduced pressure. Hexane (10 ml) was added and the solution was cooled to − 15°C. After 2 weeks, the yellow crystals were collected by filtration, washed with hexane (2 × 5 ml) and dried in a vacuum pump. Yield 80% (620 mg). m.p. > 165°C (dec.). *Anal.* Found: C, 65.41; H, 5.39; Cu, 7.70; N, 4.67. Calc. for $C_{43}H_{38}CuN_3S_2P_2$: C, 65.67; H, 5.34; Cu, 8.08; N, 4.87%. NMR (298 K): ^1H (300 MHz) δ 12.87 (br, NH, 1H), 7.69–7.12 (m, C_6H_5, 30H), 6.33 (s, C3–H, 1H) 2.32 (s, CH_3, 6H) ppm; $^{13}C\{^1H\}$ (75.4 MHz) δ 179.2, 140.2, 133.7, 129.3, 128.3, 110.8, and 22.5 ppm $^{31}P\{^1H\}$ (122.5 MHz) δ − 1.68 ppm (s). IR: 3053m, 2042 (ν NC)vs, 1617s, 1562s, 1479m, 1434s, 1226s, 1187m, 1093m, 1026w, 997w, 979w, 949w, 890w, 832w, 798w, 745s, 695s, 513s, 505m, 494m, 462w and 442w cm^{-1}.

3. Results and discussion

3.1. Synthesis of copper(I) complexes

Complex **1** was obtained in high yield (85%) in the presence of PPh_3, otherwise a mixture would result according to the following:

$$4[CuCl(PPh_3)_3] + 4NaN_3 \xrightarrow[-2PPh_3]{} \underset{68\%}{[\{Cu(N_3)(PPh_3)_2\}_2]} + 2\underset{32\%}{[Cu(N_3)(PPh_3)_3]} + 4NaCl$$

The analogue complex [$Cu(SCN)(PPh_3)_3$] could not be obtained as described above; instead, only [$\{Cu(PPh_3)_2\}_2(\mu_2\text{-}SCN)_2$] [28] was isolated.

The synthesis of **3** in melted PPh_3 proved to be an efficient one-pot preparation according to the equation below:

$$CuSCN + dmpymtH + 2PPh_3 \rightarrow [Cu(NCS)(dmpymtH)(PPh_3)_2]$$

*3.2. Crystal structures of [$Cu(N_3)(dmpymtH)(PPh_3)_2$] (**2**) and [$Cu(NCS)(dmpymtH)(PPh_3)_2$] (**3**)*

Suitable crystals were obtained from dichloromethane/hexane solutions of **2** and **3** at − 15°C, as described above. The molecules with labels for the

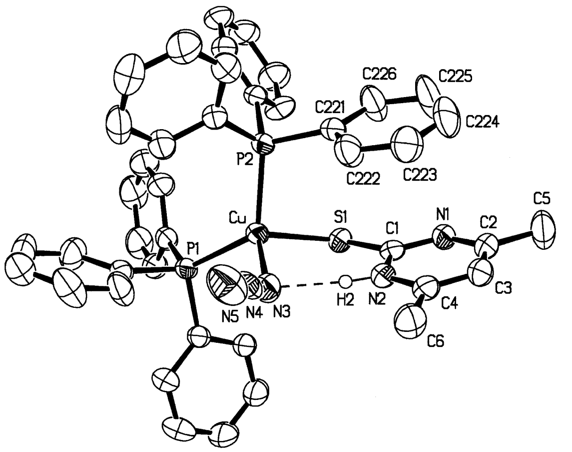


Fig. 1. ORTEP plot [37] of $[Cu(N_3)(dmpymtH)(PPh_3)_2]$ (**2**) with the atom numbering. Thermal ellipsoids are scaled at 50%. Except H(2), all other hydrogen atoms are not shown for reasons of clarity. The hydrogen bond N(2)–H(2)···N(3) is denoted by a dashed line.

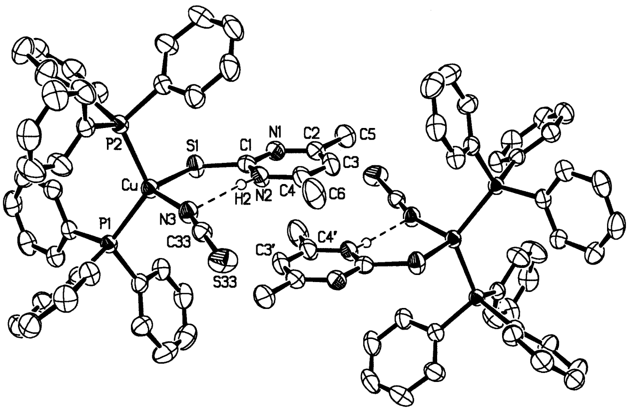


Fig. 2. ORTEP plot [37] of two neighbouring molecules in the crystal structure of $[Cu(NCS)(dmpymtH)(PPh_3)_2]$ (**3**). Except H(2), all other hydrogen atoms are not shown for reasons of clarity. The hydrogen bond N(2)–H(2)···N(3) is denoted by a dashed line.

Table 1
Crystal data and structure refinement for **2** and **3**

	2	**3**
Empirical formula	$C_{42}H_{38}CuN_5P_2S$	$C_{43}H_{38}CuN_3P_2S_2$
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Temperature (°C)	−60	−60
Unit cell parameters		
a (Å)	9.8291(6)	15.1388(17)
b (Å)	17.7041(11)	12.9769(5)
c (Å)	22.3169(18)	20.1351(7)
β (°)	101.416(8)	94.467(5)
V (Å^3)	3806.7(5)	3943.6(5)
Z	4	4
Diffractometer	Enraf–Nonius CAD4	Enraf–Nonius CAD4
Wavelength, λ (Å)	1.54184, Cu Kα	1.54184, Cu Kα
Crystal size (mm)	$0.20\times0.15\times0.10$	$0.65\times0.25\times0.20$
Method/θ range (°)	ω-scans/5–65	ω–scans/5–65
Completeness to 2θ (%)	94.1	92.1
Index ranges (h, k, l)	$-1\rightarrow10$, $0\rightarrow20$, $-26\rightarrow26$	$-1\rightarrow17$, $0\rightarrow15$, $-20\rightarrow23$
Collected reflections	7572	7246
Unique reflections/R_{int} [a]	6333/0.0432	6492/0.0276
Observed data [$I>2\sigma(I)$]	4395	5965
Absorption correction	ψ-scans [31]	ψ-scans [31]
Min./max. transmission	0.73600/0.94223	0.88588/0.95646
Extinction coefficient	not refined	0.00111(7)
Structure refinement	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Hydrogen treatment	Fourier-map	Fourier-map
Refined parameters	612	613
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0662P)^2+2.926P]$, $P=(\max F_o^2+2F_c^2)/3$	$w=1/[\sigma^2(F_o^2)+(0.0528P)^2+2.0032P]$, $P=(\max F_o^2+2F_c^2)/3$
Structure factors [$I>2\sigma(I)$] [b]	$R_1=0.0481$, $wR_2=0.1172$	$R_1=0.0340$, $wR_2=0.0932$
Goodness-of-fit, S [c]	1.020	1.062
Programs used	HELENA, PLATON [31]; SHELXS-97 [32]; SHELXL-97 [33]	HELENA, PLATON [31]; SHELXS-97 [32]; SHELXL-97 [33]

[a] $R_{int}\equiv(\Sigma|F_o^2-F_o^2(\mathrm{mean})|)/(\Sigma F_o^2)$.

[b] $R_1\equiv(\Sigma||F_o|-|F_c||)/(\Sigma|F_o|)$, $wR_2\equiv\sqrt{(\Sigma w(F_o^2-F_c^2)^2/(\Sigma w(F_o^2)^2)}$

[c] GooF: $S\equiv\sqrt{(\Sigma w(F_o^2-F_c^2)^2/(n-p)}$, $n=$ no. of reflections, $p=$ no. of parameters

main atoms are shown in Figs. 1 and 2, respectively. Parameters and conditions to the structure determination are given in Table 1. In both complexes a distorted tetrahedral coordination for the central copper atom is attained by two phosphorus atoms from triphenylphosphane, a sulphur atom from the monodentate dmpymtH and a nitrogen atom from the pseudohalide, azide in **2** and isothiocyanate in **3**.

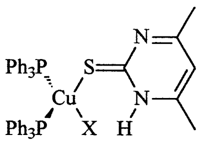
The main bond distances and angles are given in Table 2. Most values are similar in both complexes and can be considered normal. Major differences are observed for the angles P–Cu–S, that show a greater distortion from the ideal tetrahedral values in **2** than in **3** (discussed below) as well as for the Cu–N distances. The distance Cu–N(3) = 2.100 Å in **2** is appreciably longer than the mean value of 2.012 Å for copper σ-azido complexes [29], where the distance of 2.046 Å in **3** is in good agreement with the mean value of 2.045 Å for copper isothiocyanato complexes [29]. On the other hand, the Cu–S(1) distances in both complexes are nearly identical (2.372 Å in **2** and 2.371 Å in **3**) and are in accord with the Cu–S distances of 2.374 and 2.352 Å found in [CuCl(pySH)(PPh_3)$_2$] (pySH pyridine-2-thione) [2] and [CuBr(pymtH)(PPh_3)$_2$] (pymtH pyrimidine-2-thione) [6], respectively.

Table 2
Selected bond lengths (Å) and bond angles (°) for **2** and **3** [a]

	2	**3**
Bond lengths		
Cu–P(1)	2.2658(11)	2.2968(6)
Cu–P(2)	2.2799(11)	2.3112(6)
Cu–S(1)	2.3723(12)	2.3709(6)
Cu–N(3)	2.100(4)	2.0457(18)
N(3)–N(4)	1.192(5)	
N(3)–C(33)		1.162(3)
N(4)–N(5)	1.176(6)	
C(33)–S(33)		1.620(2)
S(1)–C(1)	1.701(4)	1.695(2)
C(1)–N(1)	1.347(5)	1.353(3)
C(1)–N(2)	1.358(5)	1.363(3)
C(2)–N(1)	1.331(5)	1.334(3)
C(4)–N(2)	1.355(5)	1.357(3)
C(2)–C(3)	1.387(6)	1.390(4)
C(3)–C(4)	1.359(6)	1.354(4)
N(2)–H(2)	0.92(5)	0.86(3)
H(2)···N(3)	1.87(5)	2.08(3)
N(2)···N(3)	2.786(5)	2.932(3)
Bond angles		
N(3)–Cu–P(1)	103.64(10)	107.34(5)
N(3)–Cu–P(2)	107.89(12)	105.08(6)
P(1)–Cu–P(2)	124.96(4)	122.61(2)
N(3)–Cu–S(1)	103.82(11)	108.16(5)
P(1)–Cu–S(1)	114.90(4)	109.36(2)
P(2)–Cu–S(1)	99.86(4)	103.57(2)
N(1)–C(1)–S(1)	120.9(3)	120.68(16)
N(2)–C(1)–S(1)	119.9(3)	120.18(16)
Cu–S(1)–C(1)	107.46(15)	112.20(7)
Cu–N(3)–N(4)	129.5(3)	
Cu–N(3)–C(33)		163.77(17)
N(3)–N(4)–N(5)	177.3(5)	
N(3)–C(33)–S(33)		178.86(19)
N(2)–H(2)···N(3)	175(5)	168(3)

[a] Figures in parentheses indicate the estimated standard deviation in the least significant digit.

As in **2**, also in **3** the shortest C–N and C–C distances in the coordinated dmpymtH are C(2)–N(1) and C(3)–C(4), so that they can best be represented by the following resonance structure.



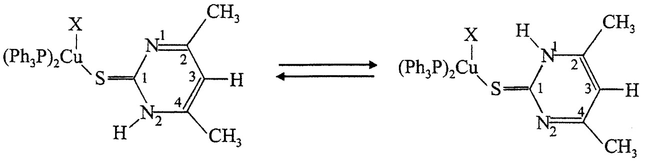
Intramolecular hydrogen bonds are observed between the atoms N(2) and N(3) in the complexes **2** and **3** with N(2)···N(3) distances of 2.786 and 2.932 Å and N(2)–H(2)···N(3) angles of 175 and 168°, respectively. The stronger hydrogen bond in **2** than in **3** is in agreement with the NMR studies.

Due to the hydrogen bond between N(2) and N(3), the atoms N(3), Cu, S(1), C(1) and N(2) are coplanar in **3** (Rms deviation 0.0753 Å) with a dihedral angle of 2,4(1)° to the dmpymtH ring. The same is not observed in **2**, which shows greater distortion from the tetrahedral coordination as a result of an intramolecular π-type stacking interaction between the dmpymtH ring and the phenyl ring bound through the carbon atom C(221) to the phosphorus atom P(2) (Fig. 1). The angle between both involved planar rings is 7.0(3)° and the closest interatomic distance is N(2)···C(222) = 3.367(6) Å.

The greater distortion due to the intramolecular π interaction in **2** in comparison with **3** can be seen in the decrease of the angle P(2)–Cu–S(1) (99.86° in **2** and 103.57° in **3**) and in the resulting increase of the angle P(1)–Cu–S(1) (114.90° in **2** and 109.36° in **3**). Intermolecular π-type stacking interactions are also observed between the dmpymtH rings from two neighbour complex molecules. In this case the interaction occurs in both complexes **2** and **3**. Fig. 2 shows the interaction between two molecules of **3**. The closest interatomic distances between the two parallel dmpymtH rings are N(1)···C(4)′ = 3.319(5) Å in **2** and C(1)···C(3)′ = 3.522(3) Å in **3**. While **3** shows a π–π-type of interaction, in **2** a π–π–π–π-type of stacking interaction is assumed. Such a stacking interaction has been reported for similar systems, for example, in crystal structures of dicopper(I) complexes of 2,2′-bipyrimidine and diphosphane ligands [30].

3.3. Infrared spectra

Complex **1** shows a strong absorption band at 2037 cm^{-1} due to $\nu(N_3^-)$ while the reported dinuclear com-



Scheme 1.

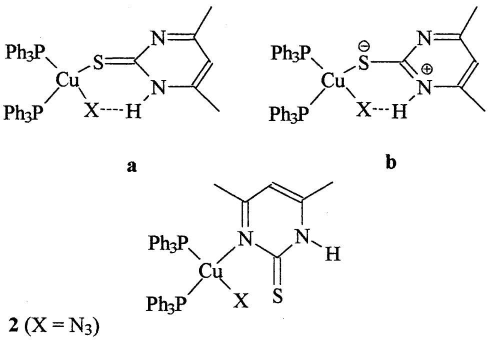
plex $[\{Cu(PPh_3)_2\}_2(\mu_2\text{-}N_3)_2]$ shows two bands at 2053 and 2002 cm^{-1} [34,35]. While **2** presents a strong band at 2034 cm^{-1}, $\nu(N_3^-)$; **3** shows a strong band at 2042 cm^{-1}, ν(NC). The compound 4,6-dimethylpyrimidine-2(1H)-thione presents a rather complicated spectrum in the range 3200–2500 cm^{-1} where C–H and N–H stretching vibrations occur. The bands in the range 2900–2500 cm^{-1} may be combination bands or may correspond to strongly hydrogen bonded NH groups as has been observed for 2-mercaptopyrimidine [36]. Those bands, although weaker, are still present on both **2** and **3**.

3.4. NMR spectroscopy

The ^{1}H and ^{13}C NMR spectra of **3** in CDCl$_3$ solution at low temperature (208 K) are consistent with a static structure as found in the crystal structure, exhibiting two carbon and proton signals for the non-equivalent methyl groups of the dmpymtH ligand. Upon raising the temperature to 253 K these signals coalesce to one, and at room temperature only one set of signals is observed. Furthermore, two distinct signals are observed for C-2 and C-4 at 208 K, whereas rapid exchange between the two is observed at higher temperatures. On the other hand, minimal change with temperature is observed for H-3, C-3 and C-1, suggesting fast tautomerization according to Scheme 1.

The tautomerization may involve a zwitterionic form of the type **b** (below) as has been demonstrated in pyridinethione complexes [2]. This interpretation is further supported by the fact that the NH proton signal, which exhibits a sharp singlet at 208 K, broadens beyond recognition upon raising the temperature.

In the case of complex **2**, however, the situation appears to be more complex. Two sets of signals (4:1) are observed for all protons and carbons of the dmpymtH ligand at 208 K (Fig. 3). This observation can be interpreted as a mixture of two respective isomers, **2a** and **2c**, as depicted below:



a **b**

2 (X = N$_3$)
3 (X = NCS)

c

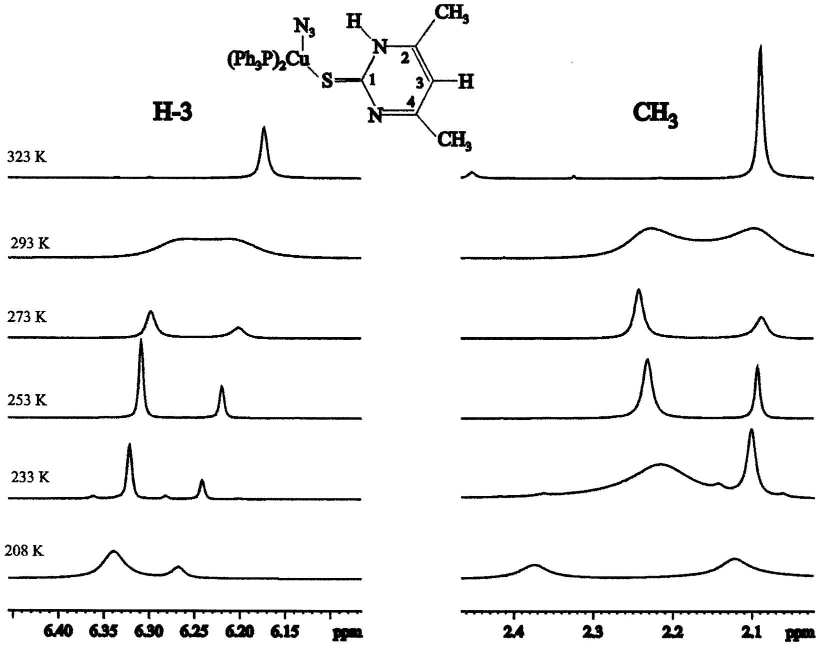


Fig. 3. Variable-temperature ^{1}H NMR spectra of **2** showing the methyl and H-3 regions of the spectrum. Two processes are taking place. As the temperature is lowered, an intermolecular process is frozen out at around 273 K, resulting in a mixture of **2a** and **2c** with a ratio around 4:1. Further lowering of the temperature also slows down the amine proton tautomerization, resulting in the split of the methyl signal. Similar behavior is observed for the corresponding ^{13}C signals. In the case of complex **3**, only isomer **a** is present and just the tautomerization process is observed.

Upon warming to 253 K the two methyl groups of **2a** coalesce in a similar fashion as observed for **3,** but two isomers are retained. Above that temperature the two isomers (**2a** and **2c**) also undergo fast exchange, resulting in only one set of signals at 323 K.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 142294 for **2** and 142295 for **3**. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Variable-temperature spectra referring to complex **3** were included to aid the reviewer's analysis.

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