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Copper(II) and nickel(II) complexes of 5-methyl-2-hydroxyacetophenone *N*(4)-substituted thiosemicarbazones

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Abstract

Mononuclear and binuclear copper(II) and nickel(II) complexes with 5-methyl-2-hydroxyacetophenone *N*(4)-substituted thiosemicarbazones have been prepared and characterized. IR and ^{1}H NMR spectra of the *N*(4)-substituted thiosemicarbazones and their metal complexes, as well as ESR spectra of the mononuclear copper(II) complexes, have been obtained. The crystal structures of 5-methyl-2-hydroxyacetophenone *N*(4)-dimethylthiosemicarbazone and a representative binuclear copper(II) complex have been acquired, and their structural features are compared to related thiosemicarbazones and previously reported binuclear copper(II) thiosemicarbazone complexes.

Keywords: Hydroxyacetophenone; Thiosemicarbazone; Copper; Nickel; Crystal structures; Metal(II) complexes

1. Introduction

Because of their potential biological activity [1], there is considerable interest in metal complexes of heterocyclic thiosemicarbazones [2], as well as salicylaldehyde and 2-hydroxyacetophenone thiosemicarbazones [3]. Either mononuclear or binuclear complexes of stoichiometry [M(ONS)L] (M=Cu, Ni; L = neutral ligand) [4], or $[M(ONS)]_2$ [5–7] have been prepared with salicylaldehyde or 2-hydroxyacetophenone thiosemicarbazones. Deprotonation of the phenoxy oxygen and loss of the N3 hydrogen of the thiosemicarbazone moiety results in dianionic ligands that coordinate via the phenoxy oxygen, imine nitrogen and thiolate sulfur atoms as shown in Fig. 1(a and b) for the two types of complexes. More recent studies have shown that palladium(II) complexes of this series of thiosemicarbazones can either be trinuclear [8], Fig. 1(c), or with one neutral thiosemicarbazone ligand and the other dianionic [9], Fig. 1(d). In view of the possible stoichiometries of complexes prepared with this series of thiosemicarbazones, we report here a study of 5-methyl-2-hydroxyacetophenone *N*(4)-methyl-, *N*(4)-dimethyl-, and 3-piperidylthiosemicarbazones, $H_25MAp4M$, $H_25MAp4DM$, and $H_25MAppip$, respectively Fig. 2, and a selection of copper(II) and nickel(II) complexes. Included are the crystal structures of $H_25MAp4DM$ and its binuclear copper(II) complex, $[Cu(5MAp4DM)]_2$.

2. Experimental

2.1. Preparation of $H_25MAp4M$, $H_25MAp4DM$, and $H_25MAppip$

The 5-methyl-2-hydroxyacetophenone *N*(4)-substituted thiosemicarbazones were prepared from 0.01 mol of 5-methyl-2-hydroxyacetophenone (Aldrich Chemical Company, Milwaukee, WI) and the desired substituted thiosemicarbazide (0.01 mol) by refluxing in 30 ml of EtOH with two drops of concentrated sulfuric acid.

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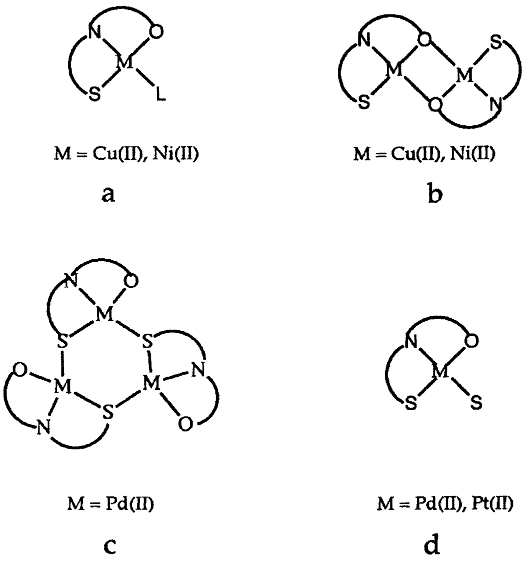

Fig. 1. Possible modes of coordination for 2-hydroxyacetophenone thiosemicarbazones

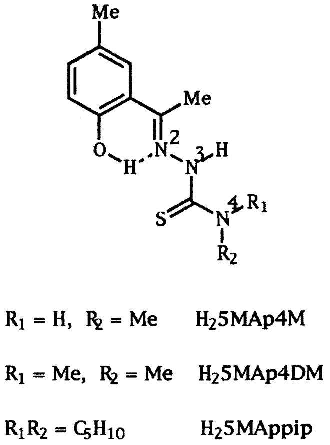

Fig. 2. $H_25MAp4M$, $H_25MAp4DM$, and $H_25MAppip$ with numbering system.

N(4)-Methylthiosemicarbazide was purchased from Aldrich and the other thiosemicarbazides were prepared following the literature procedure [10]. The melting points of the thiosemicarbazones are as follows: $H_25MAp4M$, 187–188 °C; $H_25MAp4DM$, 204–206 °C and $H_25MAppip$, 185–187 °C. IR assignments (nujol mulls, cm^{-1}): $H_25MAp4M$: ν(OH), 3385; ν(NH), 3295; ν(CN), 1605; (thioamide IV band-substantial ν(CS) contribution), 815; $H_25MAp4DM$: ν(OH), 3385; ν(CN), 1597; ν(CS), 828; $H_25MAppip$: ν(OH), 3374; ν(CN), 1567; ν(CS), 826. NMR assignments (DMSO-d_6, ppm) for $H_25MAp4M$: O*H*, 11.08; N3*H*, 10.39; C6*H*, 7.28, NCH_3, 2.99; CH_3(acetyl), 2.27; CH_3(ring), 2.22; for $H_25MAp4DM$: O*H*, 12.69; N3*H*, 9.84; C6*H*, 7.36, NCH_3, 3.29; CH_3(acetyl), 2.35; CH_3(ring), 2.22; for $H_25MAppip$: O*H*, 12.69, C6*H*, 7.31, 7.22; $H_25MAppip$ is a mixture (1:1 based on integration) of isomers and discussed later in this study. Crystals of $H_25MAp4DM$ suitable for X-ray diffraction were grown by slow evaporation of a 1:1 by volume mixture of ethanol and acetone.

2.2. Preparation of the copper(II) and nickel(II) complexes

The binuclear copper(II) and nickel(II) complexes were prepared by mixing solutions of 0.002 mol of the desired thiosemicarbazone in 30 ml of EtOH and 0.002 mol of $Ni(OAc)_2$ or $Cu(OAc)_2 \cdot H_2O$ in 20 ml of EtOH. The mixtures were refluxed for approximately 2 h, then slowly evaporated at 35 °C until sufficient solid formed. To prepare the mixed ligand complexes equimolar amounts of pyridine or bipyridine were added to the above mixtures and treated in the same manner as described. The resulting solids were filtered and washed with cold isopropanol followed by anhydrous ether. National Chemical Consulting, Inc. Tenafly, NJ, provided partial elemental analyses for the complexes. The physical and spectral methods of characterization for both the thiosemicarbazones and their metal complexes were carried out as described previously [11]. Diffraction quality crystals of $[Cu(5MAp4DM)]_2$ were obtained from an electrochemical oxidation of copper in an acetonitrile solution of $H_25MAp4DM$ followed by slow evaporation.

2.3. Crystal structure determinations

A yellow crystal of $H_25MAp4DM$ and a brown crystal of $[Cu(5MAp4DM)]_2$ were mounted on glass fibers and used for data collection on a Nonius MACH 3 diffractometer. The structures were solved by direct methods [12], which revealed the position of all non-hydrogen atoms, and refined on F^2 by a full-matrix least-square procedure using anisotropic displacement parameters [13]. The hydrogen atoms attached to carbons were located in their calculated positions and refined using a riding model; the hydrogens attached to nitrogens were found and refined isotropically. Atomic scattering factors were taken from the International Table for X-ray Crystallography [14] and molecular graphics are from Platon ($H_25MAp4DM$) [15] or ORTEP ($[Cu(5MAp4DM)]_2$) [16].

3. Results and discussion

The molecular structures of $H_25MAp4DM$ and $[Cu(5MAp4DM)]_2$ are shown in Figs. 3 and 4, respectively. Table 1 has summaries of crystal data and intensity collection for the two compounds. A selection of bond distances and angles in the thiosemicarbazone fragment and coordination sphere are listed in Tables 2

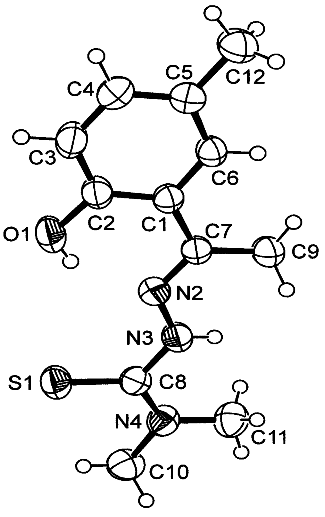

Fig. 3. View of $H_25MAp4DM$ at 50% probability showing the numbering system.

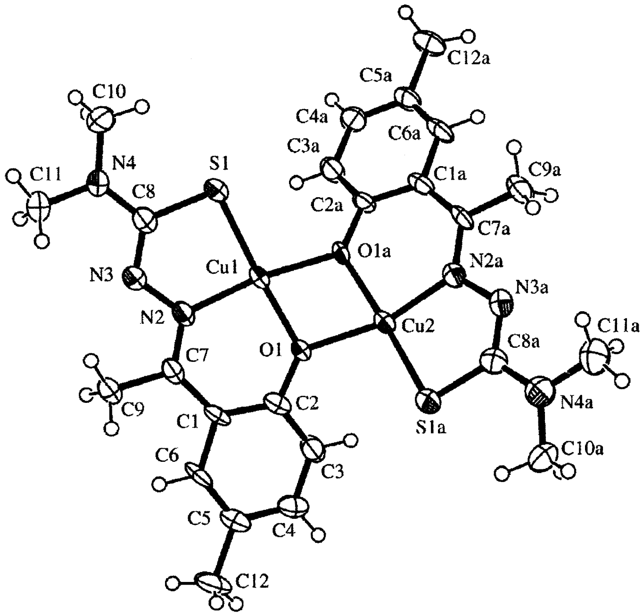

Fig. 4. View of $[Cu(5MAp4DM)_2]$ at 50% probability showing the numbering system.

and 3. Mean plane deviations, atoms showing the greatest deviation for each plane and the angles between planes are shown in Table 4.

3.1. Structure of $H_25MAp4DM$

$H_25MAp4DM$ crystallizes in the monoclinic space group $P2_1/c$ as the E-isomer with respect to the C7–N2 bond and E with respect to the N3–C8 bond, Fig. 3. This is in contrast to 5-methyl-2-hydroxyacetophenone thiosemicarbazone hydrate, $H_25MAp4DH \cdot H_2O$, which crystallizes in the monoclinic space group $C2/c$ and has a E, Z conformation with respect to the C7–N2 and N3–C8 bonds [18]. This latter arrangement, which is common in thiosemicarbazones with at least one hydrogen attached to N4 [17,18], features a weak N4–H4··· N2 intramolecular hydrogen bond that is not possible in

Table 1
Crystal data and structure refinement for $H_25MAp4DM$ and $[Cu(5MAp4DM)]_2$

Empirical formula	$C_{12}H_{17}N_3OS$	$C_{24}H_{30}Cu_2N_6O_2S_2$
Formula weight	251.36	625.74
Crystal color, habit	yellow, prism	brown, plate
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71069	1.54184
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$ (#14)	$P2_1/n$ (#14)
Unit cell dimensions		
a (Å)	8.891(3)	18.203(3)
b (Å)	7.672(4)	7.8895(15)
c (Å)	18.947(7)	18.2483(14)
β (°)	91.71(3)	94.277(7)
V (Å^3)	1291.8(4)	2613.4(6)
Z	4	4
D_{calc} (Mg m^3)	1.220	1.590
Absorption coefficient (mm^{-1})	0.235	3.781
$F(0\,0\,0)$	504	1288
Crystal size (mm)	0.26 × 0.20 × 0.14	0.20 × 0.12 × 0.02
θ Range for data collection (°)	2.15–24.65	3.31–74.89
Index ranges	$0 \le h \le 10$, $0 \le k \le 9$, $-22 \le l \le 22$	$-22 \le h \le 22$, $0 \le k \le 9$, $-22 \le l \le 0$
Reflections collected	2268	5516
Independent reflections, R_{int}	2127, 0.0085	5345, 0.1454
Absorption correction	Ψ-scans	Ψ-scans
Max and min transmission	0.9678 and 0.9414	0.9282 and 0.5185
Data/parameters	2127/176	5345/326
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0387$, $wR = 0.1085$	$R_1 = 0.0587$, $wR_2 = 0.1548$
R indices (all data)	$R_1 = 0.0460$, $wR = 0.1183$	$R_1 = 0.1540$, $wR_2 = 0.1951$
Goodness-of-fit on F^2	1.064	0.990
Largest difference peak and hole (e Å^{-3})	0.235 and −0.148	1.091 and −1.223

Table 2
Selected bond distances (Å) for $H_25MAp4DM$ and $[Cu(5MAp4DM)]_2$

Bond	$H_25MAp4DM$	$[Cu(5MAp4DM)]_2$ [a]	
C8–S1	1.686(2)	1.756(5)	1.768(6)
C7–N2	1.300(2)	1.322(6)	1.323(6)
N2–N3	1.370(2)	1.370(6)	1.380(6)
N3–C8	1.377(3)	1.319(7)	1.309(7)
C8–N4	1.339(2)	1.335(7)	1.350(7)
C2–O1	1.365(2)	1.343(5)	1.349(6)
Cu1–N2		1.931(4)	1.954(4)
Cu1–S1		2.2060(16)	2.2218(16)
Cu1–O1		1.918(3)	2.010(3)
Cu1–O2		1.956(3)	1.911(4)

[a] The second number refers to the distances about Cu2.

Table 3
Selected bond angles (°) for $H_25MAp4DM$ and $[Cu(5MAp4DM)]_2$

Angle	$H_25MAp4DM$	$[Cu(5MAp4DM)]_2$ [a]	
C1–C7–N2	115.69(15)	122.8(5)	123.0(5)
C9–C7–N2	122.86(16)	117.2(5)	116.9(5)
C7–N2–N3	118.43(15)	114.8(4)	115.1(4)
N2–N3–C8	120.37(16)	115.3(4)	115.5(5)
N3–C8–N4	114.36(16)	117.6(5)	117.5(5)
N3–C8–S1	121.33(14)	123.5(4)	124.3(4)
N4–C8–S1	124.28(14)	118.9(5)	118.2(4)
C1–C2–O1	123.58(17)	122.2(5)	121.2(5)
C3–C2–O1	117.14(17)	118.1(5)	119.2(5)
Cu1–N2–C7		126.1(4)	126.4(4)
Cu1–N2–N3		119.0(3)	118.5(3)
Cu1–S1–C8		94.0(2)	93.67(19)
N2–Cu1–S1		88.11(14)	88.00(14)
N2–Cu1–O1		94.70(17)	91.43(16)
N2–Cu1–O2		170.50(17)	162.37(17)
S1–Cu1–O1		175.20(12)	166.50(14)
S1–Cu1–O2		100.27(11)	101.91(11)
O1–Cu1–O2		76.64(14)	75.51(14)
Cu1–O1–Cu2		99.84(15)	102.03(15)

[a] The second number refers to the angles about Cu2.

$H_25MAp4DM$. The O1–H1···N2 hydrogen bonding interaction is common to salicylaldehyde and 2-hydroxyacetophenone thiosemicarbazones [18–21]. The $H_25MAp4DM$ molecule is nearly planar; the phenyl ring has a mean plane deviation of 0.0070 Å, the thiosemicarbazone moiety 0.0097 Å with N2 farthest from the mean plane, and the angle between the two mean planes is 9.25(7)°.

The C8–S1 bond distance listed in Table 2, 1.686(2) Å, is consistent with it being considered a formal double bond and comparable to 1.694(2) Å in $H_25MAp4DH$ [20]. Likewise, C7–N2, 1.300(2) Å, is consistent with substantial double bond character and similar to the bond distance of 1.289(3) Å in $H_25MAp4DH$. The C8–N4 bond, 1.339(2) Å, also has substantial double bond character although this same bond in $H_25MAp4DH$ is even shorter, 1.316(3) Å. The bond angles listed in Table 3 for $H_25MAp4DM$ are also consistent with considerable delocalization of electron density since all are within 5 of 120°, as was found for $H_25MAp4DH$ [18]. The parameters for the O1–H1···N2 hydrogen bonding interaction in $H_25MAp4DM$ are as follows: O1–H1, 0.82 Å; H1···N2, 1.87 Å; O1···N2, 2.576(2) Å; and ∠ O1–H1···N2, 144.3°. These values are comparable to those found for $H_25MAp4DH$ [18]. The closest intermolecular distances, 2.8–2.9 Å, are between hydrogens of a *N*-methyl group and O1 and N1, as well as a hydrogen of the 5-methyl group and O1. The possibility of a significant N3H3···S1 intermolecular interaction for $H_25MAp4DM$, which is found in $H_25MAp4DH$, is ruled out since H2 and S1 are more than 3.25 Å apart. Although this interaction is present in many thiosemicarbazones and thioureas, the conformation of $H_25MAp4DM$ has the acetyl methyl and one of the *N*4-methyl groups hindering an interaction by N3*H*3 of a neighboring molecule.

3.2. Structure of $[Cu(5MAp4DM)]_2$

Loss of the phenolic proton, as well as the proton from N3 of the thiosemicarbazone moiety, produces a tridentate, dianionic ligand. In the absence of a suitable neutral ligand, a binuclear complex is formed with coordination by the thiolate sulfur, imine nitrogen, and phenolate oxygen with the latter serving as a bridge to the second copper(II) center, Fig. 4. Like $H_25MAp4DM$, $[Cu(5MAp4DM)]_2$ crystallizes in the monoclinic system, but is in the $P2_1/n$ space group. The bond distances to the two copper(II) centers are somewhat different; Cu2 has significantly longer bonds with the thiolate sulfur atom, imine nitrogen atom, and bridging oxygen atom, O1, Table 2. Compared to $H_25MAp4DM$ the bond distance of C–S, which formally becomes a single bond, increases by approximately 0.07 Å while the N3–C8 (N23–C28) bond, which formally becomes a double bond, is lowered by nearly 0.06 Å in $[Cu(5MAp4DM)]_2$. Coordination of N2 causes an increase in C7–N2 bond distance by approximately 0.02 Å while coordination of O1 results in C2–O1 also decreasing by approximately 0.02 Å. The order of bond distances to the Cu1 center is $Cu1–O1 < Cu1–N2 < Cu1–O2 < Cu1–S1$, and Cu2 also has a shorter bond to the imine nitrogen than one of the oxygen donors.

Table 4
Mean planes, atoms furthest from the mean plane and angles between the mean planes for $H_25MAp4DM$ and $[Cu(5MAp4DM)]_2$

Compound	Plane	Mean deviation	Largest deviation	Angle with previous plane
$H_25MAp4DM$	C1–C2–C3–C4–C5–C6	0.0070	C1, 0.0109(0.0012)	
	C7–N2–N3–C8–N4–S1	0.0097	N2, 0.0177(0.0010)	9.25(0.07)
$[Cu(5MAp4DM)]_2$	C1–C2–C3–C4–C5–C6	0.0101	C2, 0.0152(0.0041)	
	C1A–C2A–C3A–C4A–C5A–C6A	0.0100	C2A, 0.0150(0.0040)	55.15(0.14)
	C7A–N2A–N3A–C8A–N4A–S1A	0.0056	N3A, 0.0098(0.0044)	14.80(0.22)
	C7–N2–N3–C8–N4–S2	0.0207	N2, 0.0416(0.0043)	43.01(0.11)
	O1–N2–S1–O1A	0.0016	O1, 0.0019(0.0023)	1.13(0.15)
	O1–N2A–S1A–O1A	0.0051	O1A, 0.0059(0.0023)	38.40(0.07)

Although there are significant changes in many of the thiosemicarbazone moiety bond angles on coordination, all are in the 120° range consistent with extensive delocalization. The *cis* and *trans* bond angles about the copper centers indicate a nearly square environment although Cu2 has *trans* angles that deviate from 180° to a greater extent.

The angle between the mean plane of the aryl ring and the thiosemicarbazone moiety, 14.80(0.22)° is somewhat larger than in $H_2$5MAp4DM, 9.25(0.07)°, Table 4. The angles between the mean planes of the two pyridine rings, the two thiosemicarbazone moieties and the donor atoms attached to Cu1 and Cu2 all show a large distortion from planarity. However, the small angle between the mean planes of the thiosemicarbazone moiety and the donor atoms about Cu1 indicate considerable planarity in this part of the molecule. Further data showing the difference in the two copper(II) centers is that Cu1 is out of the mean plane of donor atoms by 0.0695(0.0021) Å while Cu2 is 0.2358(0.0020) Å from its donor atom mean plane.

In contrast, the binuclear [Cu(Aphexim)]$_2$, where Aphexim is the dianion of 2-hydroxyacetophenone 3-hexamethyleneiminylthiosemicarbazone, is a symmetrical binuclear complex with a C2 rotational axis [6]. The bond distances to copper(II) in [Cu(Aphexim)]$_2$ are essentially the same as those of Cu1 in [Cu(5MAp4DM)]$_2$. In addition, the distance between the two copper(II) atoms is nearly the same in the two complexes; the distance in [Cu(5MAp4DM)]$_2$ is 3.0057(12) Å and for [Cu(Aphexim)]$_2$, 3.000(2) Å.

3.3. Physical and magnetic properties

Table 5 shows the compositions, partial elemental analyses and magnetic moments of the isolated copper(II) and nickel(II) complexes. It is expected that the binuclear copper(II) and nickel(II) complexes will be diamagnetic, as well as the brown nickel(II) thiosemicarbazone complexes based on previous studies [22]. However, the complexes prepared in the presence of 2,2′-bipyridine, [Cu_2(5MAp4DM)$_2$bipy] and [Ni_2(5MAp4DM)$_2$bipy], have some paramagnetism. For [Cu_2(5MAp4DM)$_2$bipy] this could result from a monomeric impurity or reduced electron exchange due to the two copper(II) centers not being coplanar. For [Ni_2(5MAp4DM)$_2$bipy] the bridging bipy ligand probably causes a distortion from planarity in the nickel(II) centers, which also effects the color of this complex and suggests a structure such as shown in Fig. 5. As expected, all the complexes are non-electrolytes in 10^{-3} M DMF solution.

The ^{1}H NMR data for the three thiosemicarbazones given in the Section 2 indicate that the O1–H1···N2 interaction is present in solution, as well as the solid state. In addition, N3*H* is downfield due to weak hydrogen bonding to the oxygen of the DMSO solvent. The chemical shifts of the N4CH_3 resonances in $H_2$5MAp4M and $H_2$5MAp4DM are comparable to the analogous thiosemicarbazones derived from other aldehydes and ketones [6,23]. The chemical shifts of the acetyl CH_3 resonances are upfield from those of the analogous thiosemicarbazones prepared with 2-acetylpyridine and acetylpyrazine [24,25]. The reason for two resonances for C6*H* with equivalent integration in the spectrum of $H_2$5MAppip is probably due to restricted rotation about the N3–C8 bond. Note that O*H* is a single resonance, which indicates that the isomers do not differ significantly in the O–H···N2 interaction.

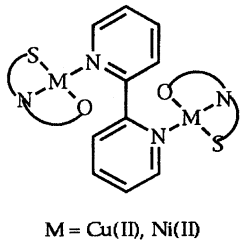

Fig. 5. Possible mode of coordination in [Cu_2(5MAp4DM)$_2$bipy] and [Ni_2(5MAp4DM)$_2$bipy].

Table 5
Colors, magnetic susceptibilities and partial elemental analyses of the copper(II) and nickel(II) complexes of 5-methyl-2-hydroxyacetophenone *N*(4)-substituted thiosemicarbazones

Compound	Color	μ_{eff}	%Found(Calc.)		
			C	H	N
[Cu(5MAp4M)]$_2$	dark brown	0	44.8(44.2)	4.5(4.4)	13.8(14.1)
[Cu(5MAp4DM)]$_2$	brown	0	46.8(46.1)	5.0(4.8)	13.4(13.4)
[Cu(5MAp4DM)py]	brown	1.5	52.6(52.1)	5.3(5.1)	14.1(14.3)
[Cu_2(5MAp4DM)$_2$bipy]	brown	0.7 [a]	52.5(52.2)	5.0(4.9)	14.2(14.3)
[Cu(5MAppip)]$_2$	dark brown	0.2 [a]	50.0(49.6)	5.1(5.6)	
[Ni(5MAp4DM)]$_2$	dark brown	0	47.6(46.8)	5.1(4.9)	13.4(13.6)
[Ni(5MAp4DM)py]	brown	0	53.3(52.7)	5.3(5.2)	14.4(14.5)
[Ni_2(5MAp4DM)$_2$bipy] H_2O	tan	1.3 [a]	51.5(51.7)	4.9(5.1)	14.3(14.2)

[a] Per metal ion.

Although isomers were not present, the crystal structures of 2-benzoylpyridine 3-piperidylthiosemicarbazone and 3-hexamethyleneiminylthiosemicarbazone showed that they were *E* and *Z*, respectively, about the N3–C8 bond [26]. In addition, the spectra of 2-hydroxyacetophenone 3-hexamethyleneiminylthiosemicarbazone shows the same behavior in $CDCl_3$ with two closely spaced resonances for OH [6].

The spectrum of $[Cu(5MAp4DM)]_2$ shows the following differences: the resonances for O*H* and N3*H* are absent, N4CH_3 is found at $\delta = 3.72$, downfield from $\delta = 3.29$ for $H_25MAp4DM$, and the acetyl CH_3 also is downfield, $\delta = 2.90$, compared to $\delta = 2.35$ for $H_25MAp4DM$. The spectrum of $[Cu_2(5MAp4DM)_2bipy]$ has the same absences and similar chemical shifts for the remaining hydrogen atoms. None of the diamagnetic nickel(II) complexes were sufficiently soluble to obtain useful ^1H NMR spectra.

The solid, binuclear copper(II) complexes are ESR silent, as expected from their diamagnetism, in agreement with previous results on similar complexes [6]. The powder spectrum for [Cu(5MAp4DM)py] has $g_{\parallel} = 2.149$ and $g_{\perp} = 2.043$ resulting in an average *g*-value of 2.078, which is comparable to 2.085 found for another $CuON_2S$ complex, a copper(II) compound with the tridentate bonding anion of 2-pyridineformamide *N*4-methylthiosemicarbazone and a monodentate acetate ligand [27]. However, as reported for other ONS dianionic ligands with phenoxy bridging, solutions of the binuclear complexes are ESR active because polar solvent molecules readily cleave the bridging bonds to form monomeric species [6,28]. When dissolved in DMF nicely resolved isotropic spectra were obtained with the previously studied binuclear complexes of the various 2-hydroxyacetophenone thiosemicarbazones [6]. In pyridine similar spectra are obtained with the present complexes; for example, for $[Cu(5MAp4DM)]_2$, $g_o = 2.097$, $A_o = 73$ G, $A_N = 17$ G and the spectra of $[Cu(5MAp4M)]_2$ and $[Cu(5MAppip)]_2$ have essentially the same values for these parameters. In these spectra three nitrogen superhyperfine lines are obtained because of coordination of the imine nitrogen, N2, suggesting that the pyridine ring does not bond coplanar with the tridentate thiosemicarbazone ligand. When $[Cu(5MAp4DM)]_2$ is dissolved in chloroform the spectrum is not as nicely resolved, but addition of pyridine produces the spectrum discussed above, but further addition of pyridine (approximately 5:1 pyridine to complex) gives a nicely resolved spectrum with $g_o = 2.104$, $A_o = 79$ G, $A_N = 14$ G with five nitrogen superhyperfine lines suggesting that a second pyridine molecule is coordinated coplanar with the thiosemicarbazone ligand. Therefore, as found previously, in pyridine and polar solvents the binuclear species is dissociated to form monomeric species, [Cu(5MAp4DM)py]. However, a second species is formed in less polar solvents in larger concentrations of pyridine; a species such as $[Cu(5MAp4DM)py_2]$ results.

3.4. Infrared spectra

Like previously studied 2-hydroxyacetophenone *N*4-substituted thiosemicarbazones and their copper(II) [6] and nickel(II) [7] complexes, ν(OH) found at approximately 3350 cm^{-1} in the thiosemicarbazones is absent in the spectra of the metal compounds. Also, coordination causes ν(CN) to shift from approximately 1600 cm^{-1} in the spectra of the thiosemicarbazones to 1550–1560 cm^{-1} and 1535–1550 cm^{-1} in the spectra of the binuclear copper(II) and nickel(II) complexes, respectively. The ν(CO) band is assigned at approximately 1255 cm^{-1} in the spectra of the thiosemicarbazones and because of coordination at 20–30 cm^{-1} lower energy in the binuclear complexes' spectra. The thioamide IV band, which has a large contribution from ν(CS) is found at approximately 820 cm^{-1} in the thiosemicarbazones' spectra and 750–760 cm^{-1} in the spectra of the complexes due to coordination of the thiolate sulfur. The ranges for ν(MN), ν(MO), and ν(MS) in the binuclear copper(II) complexes are 460–470 cm^{-1}, 420–445 cm^{-1} and 320–340 cm^{-1}, respectively, and 470–485 cm^{-1}, 435–455 cm^{-1} and 330–350 cm^{-1}, respectively for the nickel(II) complexes.

3.5. Conclusion

When 5-methyl-2-hydroxyacetophenone thiosemicarbazones react with copper(II) and nickel(II) acetate in a 1:1 molar ratio, the binuclear complexes are formed. In the presence of a neutral ligand, such as pyridine derivatives, mononuclear complexes result. In both types of compounds coordinate bonds are formed with the thiolate sulfur and imine nitrogen atoms of the thiosemicarbazone moiety, as well as the phenolate oxygen, which is the bridging atom in the binuclear complexes.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-204094 for $H_25MAp4DM$ and CCDC-204095 for $[Cu(5MAp4DM)]_2$. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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