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BINUCLEAR COPPER(II) COMPLEXES OF 2-HYDROXYACETOPHENONE ^{4}N-SUBSTITUTED THIOSEMICARBAZONES

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Abstract—Binuclear copper(II) complexes with eight different 2-hydroxyacetophenone ^{4}N-substituted thiosemicarbazones have been prepared and characterized. IR, electronic, ^{1}H NMR and ESR spectra of the complexes, as well as IR, UV and ^{1}H NMR spectra of the thiosemicarbonazones, have been obtained. The crystal structure for the copper(II) complex of 2-hydroxyacetophenone 3-hexamethyleneiminylthiosemicarbazone, $[Cu(Aphexim)]_2$, has been solved and its structural properties are compared to a recently reported nickel(II) complex. Both the thiosemicarbazones and their copper(II) complexes show no growth inhibitory activity against *Aspergillus niger*, but many have considerable activity against *Paecilomyces variotii*. Further, there is a relationship between the antifungal activity and the size of the ^{4}N substituent for both the thiosemicarbazones and their copper(II) complexes.

The crystal structures of both salicylaldehyde thiosemicarbazone[1] and 2-hydroxyacetophenone thiosemicarbazone[2] have recently been reported, and both were shown to have an *E* conformation with respect to the C=^{1}N bond (Fig. 1). Because of their potential biological activity[3] there has been considerable interest in metal complexes of both acetophenone and salicylaldehyde thiosemicarbazones; derivatives of the latter appear to have received greater attention.[4]

Copper(II) complexes of acetophenone, 4-aminoacetophenone and 4-acetylacetophenone thiosemicarbazone have been isolated with both neutral and anionic thiosemicarbazone ligands. These complexes were characterized by IR, magnetic and thermal data.[5] Also, solution thermodynamic parameters and stability constants have been determined for the copper(II) complexes of 2-hydroxyacetophenone thiosemicarbazone.[6] Copper(II) complexes, [Cu(ONS)X] (X = OAc, Cl, NO_3 and NCS), of 2,4-dihydroxyacetophenone thiosemicarbazone have been isolated and spectrally characterized.[7] Thus, there have been a number of reports concerning aromatic thiosemicarbazones in which the aromatic ring is substituted, but there have been few in which the thiosemicarbazone moiety is altered.

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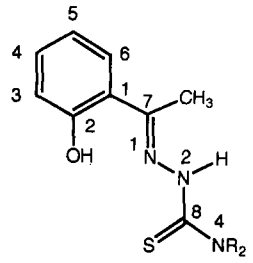

^{4}N-substituent	symbol
NHMe	H_2Ap4M
NHEt	H_2Ap4E
NHPr	H_2Ap4P
$N(Me)_2$	H_2Ap4DM
$N(Et)_2$	H_2Ap4DE
$N(Pr)_2$	H_2Ap4DP
$NCH_2(CH_2)_3CH_2$	H_2Appip
$NCH_2(CH_2)_4CH_2$	H_2Aphexim

Fig. 1. 2-Hydroxyacetophenone ^{4}N-substituted thiosemicarbazones.

One such study examined complexes of a 2-hydroxyacetophenone thiosemicarbazone, where the ^{4}N function of the thiosemicarbazone moiety is part of a morpholine ring.[8] Both the hydroxy and thiosemicarbazone ^{2}N protons are lost on formation of $[Cu(ONS)]_2$ complexes, which were characterized by spectral and magnetic measurements. Much earlier,[9] an extensive ESR spectral study of $[Cu(ONS)]_2$ complexes included 2-hydroxyacetophenone ^{4}*N*-ethylthiosemicarbazone as one of the ligands, but other spectral studies were not reported. It is these binuclear, diamagnetic complexes which are of interest to us. We report the preparation, spectral characterization and antifungal activity of a series of copper(II) complexes of 2-hydroxyacetophenone ^{4}N-substituted thiosemicarbazones, as well as the crystal structure of $[Cu(Aphexim)]_2$. Figure 1 shows the various thiosemicarbazones included in this study in their *E* configuration.

EXPERIMENTAL

The 2-hydroxyacetophenone ^{4}N-substituted thiosemicarbazones were prepared from 2-hydroxyacetophenone (Aldrich) and the desired substituted thiosemicarbazone. ^{4}*N*-methyl- and ^{4}*N*-ethylthiosemicarbazide were purchased from Aldrich Chemical Company and the remaining thiosemicarbazides were prepared following the procedure developed by Holmberg and Psilanderhielm[10] and modified by Scovill.[11] The melting points of the thiosemicarbazones are as follows: H_2Ap4M, 166–168°C; H_2Ap4E, 163–165°C; H_2Ap4P, 99–102°C; H_2Ap4DM, 195–198°C; H_2Ap4DE, 138–140°C; H_2Ap4DP, 119–121°C; H_2Appip, 180–181°C; H_2Aphexim, 177–178°C.

The binuclear copper(II) complexes were prepared by dissolving 0.002 mol of the desired thiosemicarbazone in 30 cm^3 of ethanol and 0.002 mol of $Cu(OAc)_2 \cdot H_2O$ dissolved in 20 cm^3 of ethanol was added slowly. The mixture was refluxed for *ca* 2 h, then slowly evaporated at 35°C until sufficient solid was formed, and then the mixture was filtered and washed with cold isopropanol followed by anhydrous diethyl ether. Partial elemental analysis for each of the copper(II) complexes were obtained from MicroAnalytics, Wilmington, Delaware and are shown in Table 2. The physical and spectral methods of characterization, as well as the antifungal activity, of both the thiosemicarbazones and their copper(II) complexes were carried out as described previously.[12]

The crystals were grown by slow diffusion (in a freezer) of diethyl ether into methylene chloride. The crystal, a brown arrowhead, of approximate dimensions $0.52 \times 0.44 \times 0.22$ mm, was measured on a Siemens P4 diffractometer using Mo-K_α. The unit cell parameters were obtained from least-squares refinement of the setting angles of 43 reflections in the range of $10.43 \leqslant 2\theta \leqslant 24.92$. Intensity data were collected at 20°C using an ω scan technique to a maximum of 2θ of 60°. Three reflections were chosen as intensity standards, being re-measured every 100 reflections. There was no significant variation (<2%) in the intensity of these standards. A total of 4624 reflections were measured and processed in the usual way. Of 4482 independent reflections collected, 1908 were considered to be observed $[F > 4.0\sigma(F)]$ and were used in subsequent calculations.

The structure was solved by direct methods (SIR92)[13] and refined by full-matrix least-squares (SHELXTL).[14] Complex atomic scattering factors were taken from the usual tabulations. Hydrogen atoms were included as fixed contributions and not refined. Their idealized positions were generated from the geometries about the attached carbon atoms, and they were assigned fixed thermal parameters of $U = 0.06$ Å^2. The final model converged as shown in Table 3. In the final difference Fourier map the highest peak was 0.47 e Å^{-3}.

RESULTS AND DISCUSSION

All complexes were isolated from boiling ethanolic solutions of copper(II) acetates in order to promote formation of the dianion (i.e. loss of OH

Table 1. Colours and partial elemental analyses of copper(II) complexes of 2-hydroxyacetophenone ^{4}N-substituted thiosemicarbazones

Compound	Colour	%Found (%Calc.)		
		C	H	N
$[Cu(Ap4M)]_2$	brown	42.6 (42.2)	3.8 (3.9)	14.4 (14.8)
$[Cu(Ap4E)]_2 \cdot 3H_2O$	brown	40.4 (40.5)	4.1 (5.0	12.4 (12.9)
$[Cu(Ap4P)]_2$	brown	45.9 (46.1)	4.6 (4.8)	13.4 (13.4)
$[Cu(Ap4DM)]_2$	brown	44.3 (44.2)	4.1 (4.4)	13.9 (14.1)
$[Cu(Ap4DE)]_2$	dark brown	47.3 (47.8)	5.0 (5.2)	12.0 (12.9)
$[Cu(Ap4DP)]_2 \cdot H_2O$	dark brown	49.3 (49.2)	5.5 (6.6)	11.5 (11.5)
$[Cu(Appip)]_2$	brown	50.2 (49.6)	5.0 (5.1)	12.3 (12.4)
$[Cu(Aphexim)]_2$	brown	51.4 (51.0)	5.1 (5.4)	12.0 (11.9)

and ^{2}NH protons) on complexation and, therefore, the resulting binuclear complexes.[8,9] Table 1 shows that all of the complexes have been isolated free of acetato ligands. For those complexes analysed as containing water, we have shown it to be hydrate water. Warming a sample to 60°C in a vacuum over removes the lattice water; thermograimetric analyses of samples dried in this manner show no mass loss until partial decomposition occurs well above 200°C. Further, no bands attributable to the deformation modes of coordinated water were observed in the IR spectra of the dried complexes. The isolated solids are various shades of brown; all are non-electrolytes in DMF and are diamagnetic.

Table 2 shows a summary of crystal data and X-ray analysis information, and the interactomic distances and bond angles are compiled in Table 3 for $[Cu(Aphexim)]_2$. The supplementary material contains a list of the final positional and equivalent isotropic thermal parameters of the non-hydrogen atoms. Hydrogen atom coordinates and isotropic displacement coefficients are also included in the supplementary material. A perspective view of $[Cu(Aphexim)]_2$ is shown in Fig. 2 and the packing of the molecules in Fig. 3.

The anionic Aphexim thiosemicarbazones act as tridentate ligands and coordinate to the central copper(II) atoms via the thiolato sulphur; the azomethine nitrogen, N(1); and the phenoxy oxygen atoms, which bridge to occupy the fourth coordination site (Fig. 2). There are no acetate counterions, indicating loss of both the OH and ^{2}NH hydrogens. The two halves of each binuclear molecule are related by a C_2 rotational axis and there are no relevant intermolecular interactions. The Cu—O—Cu(A)—O(A) bridging portion of the molecule shows a tetrahedral distortion with a mean plane deviation of 0.1223. This deviation from planarity is not as great as that found (0.2780)

Table 2. Crystallographic data for $[Cu(Aphexim)]_2$

Empirical formula	$C_{30}H_{38}Cu_2N_6O_2S_2$
Crystal colour, habit	Brown, arrowhead
Crystal size (mm)	$0.52 \times 0.44 \times 0.22$
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	$a = 16.515(2)$ Å
	$b = 10.213(2)$ Å
	$c = 18.192(3)$ Å
	$\beta = 93.21(2)°$
Volume	3063.6(5) Å^3
Z	4
Formula weight	705.8
Density (calc.)	1.530 g cm^{-3}
Absorption coefficient	15.64 cm^{-1}
$F(000)$	1464
Total no. of reflections measured	4624
No. of unique reflections (R_{int})	4702 (0.030)
R	0.062
R_w	0.069

for a similar binuclear nickel(II) complex involving 2-hydroxy-5-methylacetophenone ^4N-dimethylthiosemicarbazone ligands.[15] The two Cu—O bond distances of $[Cu(Aphexim)]_2$ are different [i.e. Cu—O = 1.923(4) and Cu(A)—O = 1.967 (4) Å]; a series of binuclear copper(II) complexes involving methoxy and phenoxy bridging oxygens with the latter a part of a macrocyclic ligand have bond lengths from the two copper atoms to the phenoxy oxygen of 1.954 and 1.962 Å.[16] Other Cu—O_2—Cu systems with phenoxy bridges have much greater differences in the bond lengths, 1.926 and 2.265 Å,[17] suggesting that the phenoxy bridging for $[Cu(Aphexim)]_2$ is rather strong. Recently, a binuclear copper(II) complex of 2,6-bis(aminomethyl)-4-methylphenol was found to have Cu—O bond dis-

Table 3. Bond lengths (Å) and bond angles (°) for $[Cu(Aphexim)]_2$

Cu—S(1)	2.200(2)	Cu—O(1)	1.923(4)
Cu—N(1)	1.938(5)	Cu—CuA[a]	3.000(2)
Cu—O(1A)	1.967(4)	S(1)—C(8)	1.750(7)
O(1)—C(2)	1.363(7)	O(1)—CuA	1.967(4)
N(1)—N(2)	1.374(7)	N(1)—C(7)	1.306(8)
N(2)—C(8)	1.313(9)	N(3)—C(8)	1.348(9)
N(3)—C(9)	1.465(10)	N(3)—C(14)	1.473(10)
C(1)—C(2)	1.403(9)	C(1)—C(6)	1.417(9)
C(1)—C(7)	1.476(9)	C(2)—C(3)	1.387(10)
C(3)—C(4)	1.358(10)	C(4)—C(5)	1.382(12)
C(5)—C(6)	1.349(11)	C(7)—C(15)	1.506(10)
C(9)—C(10A)	1.452(19)	C(9)—C(10B)	1.413(30)
C(10A)—C(11)	1.414(21)	C(10B)—C(113)	1.576(30)
C(11)—C(12)	1.330(17)	C(12)—C(13)	1.446(17)
C(13)—C(14)	1.499(12)		

S(1)—Cu—O(1)	166.1(1)	S(1)—Cu—N(1)	88.5(2)
O(1)—Cu—N(1)	93.0(2)	S(1)—Cu—O(1A)	101.8(1)
O(1)—Cu—O(1A)	77.2(2)	N(1)—Cu—O(1A)	169.5(2)
CuA—Cu—O(1A)	39.0(1)	CuS(1)—C(8)	93.3(2)
Cu—O(1)—C(2)	122.4(4)	Cu—O(1)—CuA	100.9(2)
C(2)—O(1)—CuA	131.0(4)	Cu—N(1)—N(2)	118.5(4)
Cu—N(1)—C(7)	125.6(4)	N(2)—N(1)—C(7)	115.8(5)
N(1)—N(2)—C(8)	114.5(5)	C(8)—N(3)—C(9)	122.7(6)
N(1)—N(2)—C(8)	120.3(6)	C(9)—N(3)—C(14)	117.0(6)
C(2)—C(1)—C(6)	115.9(6)	C(2)—C(1)—C(7)	125.0(5)
C(6)—C(1)—C(7)	119.1(6)	O(1)—C(2)—C(1)	120.7(6)
O(1)—C(2)—C(3)	119.3(6)	C(1)—C(2)—C(3)	120.0(6)
C(2)—C(3)—C(4)	121.4(7)	C(3)—C(4)—C(5)	120.2(7)
C(4)—C(5)—C(6)	118.9(7)	C(1)—C(6)—C(5)	123.4(7)
N(1)—C(7)—C(15)	122.2(6)	N(1)—C(7)—C(1)	118.4(6)
C(1)—C(7)—C(15)	119.3(5)	S(1)—C(8)—N(2)	125.0(5)
S(1)—C(8)—N(3)	118.4(5)	N(2)—C(8)—N(3)	116.6(6)
N(3)—C(9)—C(10A)	113.7(9)	N(3)—C(9)—C(10B)	118.8(13)
C(9)—C(10A)—C(11)	122.2(13)	C(9)—C(10B)—C(11)	114.1(18)
C(10A)—C(11)—C(12)	135.1(12)	C(10B)—C(11)—C(12)	117.4(14)
C(11)—C(12)—C(13)	130.4(12)	C(12)—C(13)—C(14)	116.0(8)
N(3)—C(14)—C(13)	113.4(7)		

[a] Non-bonding distance.

tances of 1.929 Å and it has a very similar separation of the two copper atoms (see below).[18] The short bridging distances for $[Cu(Aphexim)]_2$ probably cause other parts of the molecule to have greater distortion than is normally found in thiosemicarbazone complexes. For example, the mononuclear copper(II) complexes having tridentate ONS ligands are considerably more planar[19] than $[Cu(Aphexim)]_2$. Also, the Cu—S and Cu—^{1}N bond lengths are shorter for $[Cu(Aphexim)]_2$ than is found in the monomeric thiosemicarbazone complexes.[20] To our best knowledge, this is the shortest Cu^{II}—S bond [2.200(2) Å] reported to date; this bond is generally found in the range 2.225–2.290 Å for monomeric copper(II) complexes (Table 5).

The distance between the Cu—Cu atoms in the binuclear copper(II) complex of 2,6-bis(aminomethyl)-4-methylphenol[18] is 3.013(1) Å, in a representative of the phenoxy oxygen, methoxy oxygen bridged complex[16] it is 2.937(2) Å, and $[Cu(Aphexim)]_2$ has a non-bonding Cu—Cu distance of 3.000(2) Å. All three are greater than the distance found for acetato type bridging of copper(II) centres; recent reports indicate a distance of 2.644(4) and 2.647(4) Å.[21] As in other complexes involving phenoxo-bridged metal(II) centres,[16–18] the

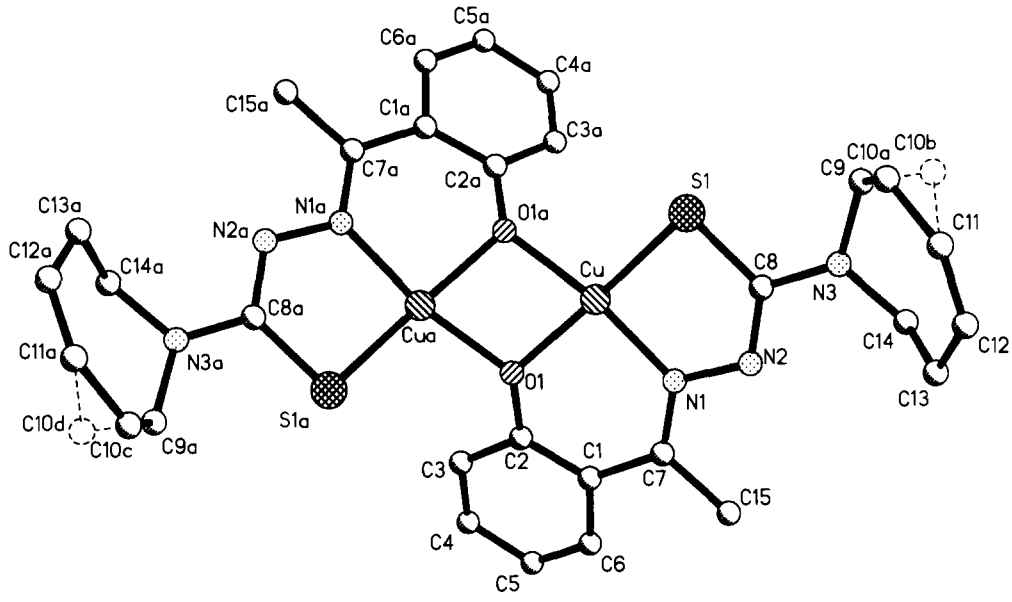

Fig. 2. ORTEP diagram for $[Cu(Aphexim)]_2$.

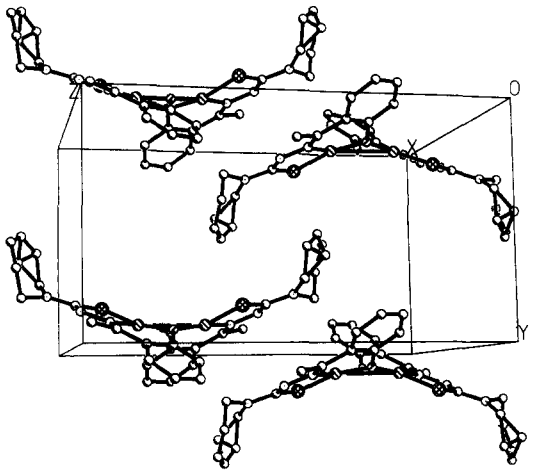

Fig. 3. Packing arrangement for $[Cu(Aphexim)]_2$.

geometry about each copper atom is not planar. The mean plane deviation from the Cu—O(1)—S—N(1)—O(1A) plane is 0.131, with O(1A) 0.360(4) above the mean plane. Also, the five-membered [Cu—S—C(8)—N(2)—N(1)] and six-membered [Cu—N(1)—C(7)—C(1)—C(2)—O(1)] chelate rings deviate considerably from planarity; the mean deviation plane for the two rings is 0.131 and 0.136, respectively. Further, the thiosemicarbazone moiety, which is in contrast to complexes of 2-acetylpyridine 3-hexamethyleneiminylthiosemicarbazone,[20] shows a clear distortion based on the angle between the two chelate rings. Also, there is distortion from planarity between the aromatic ring and the thiosemicarbazone moiety, and the hexamethyleneiminyl rings are bent away from the remainder of the thiosemicarbazone moieties, as has been noted before in thiosemicarbazone complexes involving this function.[20]

A comparison of the thiosemicarbazone moiety bond distances (Table 4) of $[Cu(Aphexim)]_2$ to those of the uncoordinated 2-hydroxyacetophenone thiosemicarbazone, H_2Ap4DH,[2] shows that coordination lengthens the $C = {}^1N$ bond slightly [1.306(8) and 1.297(3) Å, respectively] and the ${}^9C = S$ bond substantially [1.750(7) vs 1.692(2) Å, respectively], as would be expected on coordination of the azomethine nitrogen and thiol sulphur. The other bond distances of the thiosemicarbazone moiety listed in Table 4 are all decreased by 0.010–0.020 Å on coordination. The change of $C—{}^1N$ is considerably larger on coordination to the nickel(II) centre in $[Ni(DMAp4DM)]_2$[15] compared to H_2Ap4DH,[2] but the change in ${}^9C=S$ is slightly less. All metal–ligand bonds are considerably shorter for $[Ni(DMAp4DM)]_2$,[15] indicating stronger bonding to a nickel(II) centre, as was observed earlier for [Cu(Lhexim)Br] and [Ni(Lhexim)Br].[20] The stronger bonding of the thiol sulphur to nickel(II) compared to copper(II), but similarity of the ${}^9C=S$ bonds shown by the two sets of complexes in Table 4, suggests that there is considerably more π-back-bonding to the C—S bond on the nickel(II) ion. The greater π-back-bonding for the nickel(II) complexes is apparently not the result of a difference in the M—S—${}^9C$ bond angles for the two metal ions, since the angles listed in Table 4 are similar for both sets of complexes. $[Cu(Aphexim)]_2$ does have smaller bond angles (O—M—${}^1N$ and S—M—${}^1N$)

for its bichelate system than the binuclear nickel(II) complex, (Ni(DMAp4DM]$_2$.[15] Finally, it is anticipated that the binuclear copper(II) complex will have a shorter metal–sulphur bond distance, just as [Ni(DMAp4DM)]$_2$[15] has a shorter Ni—S bond than [Ni(Sa4Ph)(NH$_3$)].[22]

Table 5 shows the IR assignments for the thiosemicarbazone moiety and metal–ligand bands. On coordination of the azomethine nitrogen, $\nu(^7C{=}^1N)$ shifts to lower frequencies by 20–40 cm^{-1},[23] but with loss of the proton from ^2N, a new band due to $\nu(^2N{=}^9C)$ occurs in this same spectral region for these complexes. We have assigned the band at *ca* 1590 cm^{-1} to $\nu(^2N{=}^9C)$, and $\nu(^7C{=}^1N)$ to the band shifting from *ca* 1600 cm^{-1} in the uncomplexed thiosemicarbazones' spectra to *ca* 1570 cm^{-1} in the complexes' spectra. Coordination of the azomethine nitrogen is also consistent with the presence of a band at 450–480 cm^{-1}, assignable to ν(CuN) for these complexes.[24] On loss of the ^{2}NH hydrogen, coordination via the thiolate sulphur is indicated by a decrease in the frequency (80–100 cm^{-1}) of the thioamide IV band found at *ca* 840 cm^{-1} in the uncomplexed thiosemicarbazones' spectra and also by the presence of a band assignable to ν(CuS) in the 310–350 cm^{-1} range[25] in the complexes' spectra. The phenolic oxygen, on loss of the OH proton, occupies the third and fourth (through bridging) coordination sites. This causes ν(CO) to shift to higher wavenumbers by 60–80 cm^{-1} from its position at *ca* 1250 cm^{-1} in the thiosemicarbazones' spectra, which is consistent with a bridging phenolic oxygen.[26] A band in the 420–460 cm^{-1} range in the spectra of the complexes is assignable to ν(CuO) for the bridging phenolato oxygen.[27]

The ^{1}H NMR spectral assignments for the thiosemicarbazones are included in Table 6. The potential for hydrogen bonding of the ring OH and/or the ^{2}NH allows for the possibility of different isomers[12] for the various thiosemicarbazones, depending on the electronic and steric effects. The spectrum of H$_2$Ap4M indicates an absence of hydrogen bonding with signals for OH, ^{2}NH and ^{4}NH found at δ

Table 4. Comparison of copper-donor atom bond lengths (Å) and bond angles (°) for thiosemicarbazone copper(II) complexes and complexes containing phenoxy bridging groups

Compound	C=^{1}N	^{1}N—^{2}N	^{2}N—^{9}C	^{9}C—S	^{3}N—^{9}C	Ref.
H$_2$Sa4DH	1.276(3)	1.380(4)	1.346(4)	1.689(4)	1.317(4)	1
H$_2$ApDH	1.297(3)	1.392(3)	1.334(3)	1.692(2)	1.322(3)	2
[Cu(Aphexim)]$_2$	1.306(8)	1.374(7)	1.313(8)	1.750(7)	1.313(9)	[a]
[Ni(DMAp4DM)]$_2$	1.325(5)	1.397(5)	1.298(5)	1.744(6)	not	15
	1.317(5)	1.394(5)	1.317(5)	1.736(5)	reported	
[Ni(Sa4Ph)(NH$_3$)]	1.316(10)	1.393(7)	1.333(10)	1.717(9)	1.357(10)	22
[Cu(Lhexim)Br]	1.275(9)	1.373(7)	1.301(9)	1.759(6)	1.377(9)	20
[Ni(Lhexim)Br]	1.33(1)	1.37(1)	1.31(1)	1.76(1)	1.33(1)	20

Compound	M—S	M—^{1}N	M—O	Ref.
[Cu(Aphexim)]$_2$	2.200(2)	1.938(5)	1.923(4)	[a]
			1.967(4)	
[Ni(DMAp4DM)]$_2$	2.129(1)	1.855(5)	1.912(4)	15
	2.123(1)	1.860(4)	1.898(4)	
[Ni(Sa4Ph)(NH$_3$)]	2.166(2)	1.844(7)	1.858(6)	22
[Cu(Lhexim)Br]	2.236(3)	1.963(5)		20
[Ni(Lhexim)Br]	2.155(4)	1.857(8)		20

Compound	S—M—O	S—M—^{1}N	O—M—^{1}N	M—S—^{9}C	M—^{1}N—^{2}N	Ref.
[Cu(Aphexim)]$_2$	166.1(1)	88.5(2)	93.0(2)	93.3(2)	118.5(4)	[a]
[Ni(DMAp4DM)]$_2$	173.5(1)	89.2(2)	96.6(2)	94.8(1)	119.7(3)	15
	173.1(1)		96.4(1)	95.1(1)	120.0(3)	
[Ni(Sa4Ph)(NH$_3$)]	176.0(2)	87.7(2)	96.2(3)	95.9(3)	121.5(5)	22
[Cu(Lhexim)Br]		85.1(2)		94.5(2)	122.7(4)	20
[Ni(Lhexim)Br]		87.9(3)		94.8(4)	122.2(7)	20

[a] This work.

Table 5. IR assignments (cm^{-1}) for the 2-hydroxyacetophenone ^{4}N-substituted thiosemicarbazones and their copper(II) complexes

Compound	ν(CN)	ν(CO)	ν(CS)	ν(CuN)	ν(CuO)	ν(CuS)
H_2Ap4M	1600 m	1220 s	821 sh			
[Cu(Ap4M)]$_2$	1615 sh 1570 sh	1170 m	732 m	460 m	425 m	354 w
H_2Ap4E	1598 sh	1230 sh	808 sh			
[Cu(Ap4E)]$_2$	1595 s 1570 s	1150 s	744 s	485 m	445 m	313 sh
H_2Ap4P	1615 1595 sh	1218 sh	817 s			
[Cu(Ap4P)]$_2$	1598 s 1573 sh	1150 s	736 s	482 m	456 m	353 w
H_2Ap4DM	1605 sh	1218 sh	813 m			
[Cu(Ap4DM)]$_2$	1597 s 1568 s	1140 s	732 s	453 m	420 w	326 sh
H_2Ap4DE	1604 sh	1220 m	818 sh			
[Cu(Ap4DE)]$_2$	1595 sh 1565 sh	1135 s	745 s	475 m	445 sh	315 sh
H_2Ap4DP	1605 sh	1250 s	835 sh			
[Cu(Ap4DP)]$_2$	1594 s 15568 s	1208 m	748 s	485 sh	444 sh	316 w
H_2Appip	1595 sh	1236 s	837 sh			
[Cu(Appip)]$_2$	1595 s 1568 s	1140 s	752 s	478 m	453 m	315 m
H_2Aphexim	1598 sh	1220 s	835 sh			
[Cu(Aphexim)]$_2$	1593 s 1568 s	1138 s	750 s	476 w	451 m	304 w

10.78, 8.83 and 6.92, respectively. However, the spectrum of H_2Ap4DM shows a strong signal at δ 12.54, which integrates for nearly one hydrogen, and a weaker signal at δ 12.22, that are both assignable to a hydrogen bonded OH. Further, ^{2}NH of H_2Ap4DM is found upfield at δ 8.27 from its position of δ 8.83 in the spectrum of H_2Ap4M. Similarly, H_2Ap4DE shows the OH peak at δ 12.53 and the ^{2}NH peak at δ 8.35, consistent with the presence of a single hydrogen bonding (i.e. OH) isomer. Larger ^{4}*N*-dialkyl- (e.g. H_2Ap4DP) and 3-azacyclothiosemicarbazones (e.g. H_2Appip, H_2Aphexim) also show single OH peaks, consistent with the presence of a single hydrogen bonding isomer. H_2Ap4P, like H_2Ap4M, is present in solution as a non-hydrogen bonding isomer, but H_2Ap4E shows peaks consistent with about one-third being a hydrogen bonding isomer (i.e. OH). Complete ^{13}C NMR spectral assignments for the thiosemicarbazones will be reported[28] as a part of our study of the analogous binuclear nickel(II) complexes, which gave reasonable ^{13}C spectra. We were unable to obtain suitable ^{13}C NMR spectra for the binuclear copper(II) complexes.

The ^{1}H NMR spectral assignments for the copper(II) thiosemicarbazone complexes are included in Table 6. The signals for OH and ^{2}NH are absent from the spectra, as expected, because of their loss on complex formation. There is considerable shifting of the signals for the ring protons in the spectra of the complexes compared to their positions for the uncomplexed thiosemicarbazones, indicating coordination via the phenoxy oxygen. The loss of electron density on complexation is most significant for those carbons *ortho* (^{6}C) and *para* (^{4}C) to the phenoxy oxygen; their protons show large downfield shifts, but only a small downfield shift occurs for ^{3}CH, with a small upfield shift for ^{5}CH. The upfield shift for ^{5}CH, which would be expected to be least affected by coordination of the phenoxy oxygen and azomethine nitrogen, is probably a result of π-back-bonding. The large upfield shift of $^8CH_3$, which occurs on coordination of the azomethine nitrogen, must be due to considerable π-back-bonding by the copper(II) to the π^* orbital of the azomethine function. There is only a small effect on ^{4}NH of H_2Ap4M, H_2Ap4E and H_2Ap4P on complexation and the same is true for the protons on α, β-carbons attached to ^{4}N for this entire series of complexes. For example: H_2Ap4E [δ 3.78(2), 1.31(3) for α and β hydrogens, respectively, of the ethyl group], [Cu(Ap4E)]$_2$ [δ 3.58(2), 1.50(3)], H_2Ap4DP [δ 3.68(4), 1.77(4), 1.00(6) for α, β and γ hydrogens of the propyl groups] and [Cu(Ap4DP)]$_2$ [δ 3.73(4), 1.94(4), 0.91(6)]. Some of the shifting of peaks in the chloroform spectra of the copper(II) complexes from their positions in the corresponding uncoordinated thiosemicarbazone spectrum may be due to monomer species appearing in this solvent when studied by ESR (see below).

Each thiosemicarbazone and copper(II) complex has a ring $\pi \rightarrow \pi^*$ band at *ca* 40,000 cm^{-1} and an $n \rightarrow \pi^*$ band at *ca* 33,000 cm^{-1} (Table 7). The

Table 6. ^{1}H NMR ($CDCl_3$) assignments of 2-hydroxyacetophenone ^{4}N-substituted thiosemicarbazones

Compound	OH	^{3}CH	^{4}CH	^{5}CH	^{6}CH	^{8}CH	^{2}NH
H_2Ap4M[a]	10.78	6.98	7.32	6.93	7.47	2.39	8.83
H_2Ap4E[b]	10.77 (62.2%)	6.99	7.32	6.82	7.58	2.38	8.63
	12.60 (37.8%)	6.93	7.25	6.77	7.49		8.33
H_2Ap4P[c]	10.83	6.97	7.30	6.84	7.46	2.39	8.79
H_2Ap4DM	12.54 (94.3%)	7.00	7.27	6.85	7.37	2.28	8.27
	12.22 (5.7%)						
H_2Ap4DE	12.53	7.03	7.28	6.86	7.40	2.17	8.35
H_2Ap4DP	13.26 (37.7%)	7.03	7.27	6.95	7.66	2.29	8.35
	12.55 (62.3%)		7.39	6.86			
H_2Appip	12.10	6.98	7.28	6.88	7.42	2.32	8.22
H_2Aphexim	12.68 (85.4%)	7.01	7.26	6.83	7.36	2.28	8.36
	12.64 (14.6%)					2.17	8.30
$[Cu(Ap4M)]_2$[d]							
$[Cu(Ap4E)]_2$		7.72	9.57	6.27	9.90	0.25	
$[Cu(Ap4P)]_2$		7.53[e]	9.75	6.18	10.1	0.05	
$[Cu(Ap4DM)]_2$		7.18[e]	9.21	6.35	9.68	0.30	
$[Cu(Ap4DE)]_2$		7.19[e]	9.19	6.35	9.67	0.27	
$[Cu(Ap4DP)]_2$		7.10[e]	9.16	6.36	9.65	0.27	
$[Cu(Appip)]_2$		7.20[e]	9.25	6.33	9.63	0.26	
$[Cu(Aphexim)]_2$		7.15	9.18	6.34	9.64	0.27	

[a] ^{4}N—H, δ 6.85.
[b] ^{4}N—H, δ 6.82, 6.78.
[c] ^{4}N—H, δ 6.84.
[d] Insufficiently soluble in $CDCl_3$ and unable to record acceptable spectrum in DMSO.
[e] Broad.

second $n \rightarrow \pi^*$ band, which is found below 30,000 cm^{-1} in the uncomplexed thiosemicarbazones' spectra, merges with the first $n \rightarrow \pi^*$ band in the spectra of the copper(II) complexes. This band, which involves transitions within the thiosemicarbazone moiety (mainly C=^{1}N, C=S groups), is weakened and shifts to higher energy on complexation. Two ligand-to-metal charge transfer bands are found in the 26,000–28,000 and 21,000–23,000 cm^{-1} ranges. In accordance with studies of previous copper(II) thiosemicarbazone complexes,[29] the higher energy band is assigned to S$\rightarrow$Cu^{II} transitions. Its position is dependent on the steric requirements of the ^{4}N substituents such that thiosemicarbazones with bulkier ^{4}N substituents have this band at somewhat higher energies. The band in the 21,000–23,000 cm^{-1} range involves bridging phenoxy O $\rightarrow$ Cu^{II} transitions[30] and indicates this bridging function. Each complex has a broad *d–d* combination band that appears as a shoulder on the intraligand and charge transfer bands. With increasing size of the ^{4}N substituent, the *d–d* band maximum is found at lower energy.

The solid copper(II) complexes are ESR silent at both room and liquid nitrogen temperatures, as is expected from their diamagnetic nature and in agreement with previous results.[9] However, as has been found for other ONS dianionic ligands with phenoxy bridging, solutions of these complexes do provide ESR spectra because polar solvent molecules, L, can readily cleave the bridging bonds to give monomeric [Cu(ONS)L] complexes.[9,31] ESR spectral studies of copper(II) complexes of tridentate Schiff bases with ONO donor sets suggested that the polar solvent molecules (coordinating via a nitrogen or oxygen donor atom) occupy a non-equatorial position.[32] More recently, a similar solution ESR study has been reported[33] involving dimeric copper(II) complexes of salicylaldehyde and 2-hydroxynaphthaldehyde thiosemicarbazones and ^{4}*N*-phenylthiosemicarbazones (i.e. Sa4DH, Na4DH, Sa4Ph and Na4Ph using our symbolism). There is little variation in the ESR parameters for the four thiosemicarbazone complexes studied by Jezierska,[33] who employed DMF, DMSO and pyridine as solvents. A selection of her reported values are included in Tables 8 and 9 for comparison.

The results of our room temperature ESR study

Table 7. Solid state electronic spectra (cm^{-1}) of the 2-hydroxyacetophenone thiosemicarbazones and thier copper(II) complexes

Compound	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	L → M	$d \rightarrow d$
H_2Ap4M	40,160	33,900 29,500		
H_2Ap4E	41,150	33,000 29,500		
H_2Ap4P	42,740	33,450 29,590		
H_2Ap4DM	40,160	34,970 29,850		
H_2Ap4DE	42,190	33,330 29,070		
H_2Ap4DP	41,150	34,010 29,240		
H_2Appip	43,290	34,130 28,570		
H_2Aphexim	37,880	33,220 29,500		
$[Cu(Ap4M)]_2$	43,100	33,330	26,320 22,780	16,670 sh
$[Cu(Ap4E)]_2$	41,670	33,780	26,390 22,120	16,080 sh
$[Cu(Ap4P)]_2$	43,480	34,480	27,700 22,620	16,670 sh
$[Cu(Ap4DM)]_2$	41,670	33,330	27,030 21,740	15,870 sh
$[Cu(Ap4DE)]_2$	43,480	33,330	26,040 23,360	15,600 sh
$[Cu(Ap4DP)]_2$	42,020	33,900	26,320 22,220	16,130 sh
$[Cu(Appip)]_2$	41,670	33,330	27,550 22,220	15,920 sh
$[Cu(Aphexim)]_2$	40,000	31,750	27,700 21,370	15,360 sh

of three representative compounds {i.e.[Cu(Ap4M)]$_2$, [Cu(Ap4DM)]$_2$ and [Cu(Appip)]$_2$} are also included in Table 8. Similar to the related compounds studied before,[9,33] well resolved spectra with four copper hyperfine lines and three superhyperfine lines due to the azomethine nitrogen are observed in DMF (Fig. 4a). Similar spectra are recorded when these three complexes are dissolved in DMSO and pyridine, although the resolution is not as good as in DMF. In all three solvents the spectra are centred at g_o *ca* 2.090, with A(Cu) *ca* 67 G and A(N) *ca* 18 G, and these values are relatively constant for the three representative complexes. It is most likely that the species is [Cu(ONS)L] {or [Cu(ONS)L$_2$]}, as suggested previously,[9,33] and since superhyperfine coupling by a second nitrogen is not observed in pyridine solution, the suggestion of Jezierska[33] that the solvent molecule(s) are not coplanar with the ONS bichelate rings seems quite reasonable. Both [Cu(Ap4M)]$_2$ and [Cu(Appip)]$_2$ were sufficiently soluble in a much less polar solvent, chloroform, and allowed a weak spectrum with a lower g_o (i.e. *ca* 2.075), larger A(Cu) (i.e. *ca* 77 G) and smaller A(N) (i.e. *ca* 15 G) to be recorded (Fig. 4b). Chloroform is a rather unlikely ligand because of its poor donicity and might promote interaction between binuclear complexes. This could be the cause of the considerably lower g-values found in chloroform. Alternatively, lower g-values could be attributed to a small amount of a sulphur bridged binuclear complex, which is the more soluble species in chloroform and is paramagnetic. The additional sulphur in the coordination sphere of each copper(II) would be consistent with lower g-values.

The addition of pyridine to a DMF or DMSO solution of these complexes has no effect on the spectra until the complex-to-pyridine ratio reaches 1 : 5, and a spectrum with five superhyperfine lines (two nitrogen donor atoms) is observed (Fig. 4c). The hyperfine coupling of the second nitrogen arises from the planar coordination of a pyridine molecule. The spectrum has g_o *ca* 2.085, with A(Cu) *ca* 78 G and A(N) *ca* 14 G. The same spectrum can be observed by adding pyridine to chloroform solutions of these complexes and the pyridine increases the solubility of the complexes in chloroform, as would be expected. This species, while having a pyridine molecule added co-planar to the ONS bichelate system, must have considerable axial bonding from the polar solvents (i.e. DMF, DMSO or pyridine in chloroform), which causes the relatively large g_o-value.

Table 9 contains the ESR parameters for frozen solutions of [Cu(Ap4M)]$_2$, [Cu(Ap4DM)]$_2$ and [Cu(Appip)]$_2$, as well as 2% copper doped into [Ni(Ap4DM)]$_2$.[28] In polar solvents $g_\parallel$ is in the 2.180–2.210 range for the three complexes, and $A_\parallel$ is 170–190 G. In chloroform, Cu$_2$(Ap4M)$_2$ has $g_\parallel = 2.149$, suggesting much stronger planar bonding and weaker axial bonding in this solvent. Intermediate between this is $g_\parallel = 2.164$ found for [Cu(Ap4DM)]$_2$ doped into [Ni(Ap4DM)]$_2$, which is the only successful doping that we were able to accomplish with this set of complexes. $A_\parallel$ is essentially the same in polar solvents, non-polar solvents

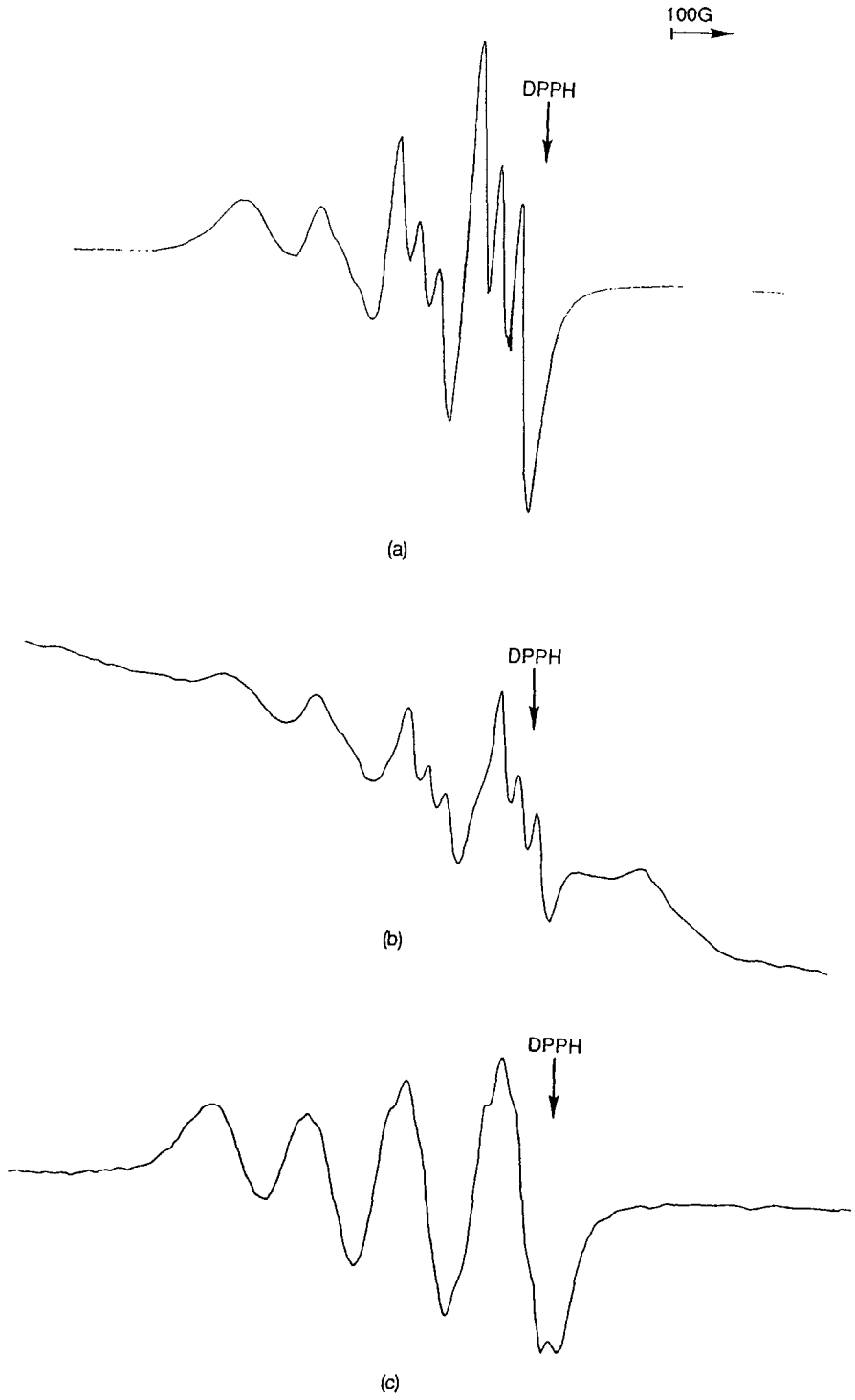

Fig. 4. Room temperature ESR spectra of $[Cu(AP4DM)]_2$ in DMF (a), $CHCl_3$ (b) and DMF (c) with 5:1 pyridine–$[Cu(ap4DM)]_2$ added.

and the analogous nickel(II) binuclear complex. On addition of pyridine to polar solvent solutions, there is generally a small increase in $g_{\|}$, suggesting that pyridine is a better axial donor than DMF or DMSO. When pyridine is added to $CHCl_3$ there is a large increase in $g_{\|}$, as would be expected due to the much stronger axial interaction.

Table 10 shows the growth inhibitory activity of the uncomplexed thiosemicarbazones and their copper(II) complexes against *Paecilomyces variotii*.

Table 8. Room temperature ESR spectral parameters of the copper(II) complexes of 2-hydroxyacetophenone thiosemicarbazones in different solvents

Complex	Solvent	Cu : py	g_o	A_o (G)	A_N (no.)
$[Cu(Ap4M)]_2$	$CHCl_3$		2.076	76	16 (1)
	$CHCl_3$–py	2 : 1	2.084	80	13 (2)
	$CHCl_3$–py	1 : 1	2.086	80	12 (2)
	$CHCl_3$–py	1 : 2	2.083	81	12 (2)
	py		2.097	73	16 (1)
	DMSO		2.092	65	17.5 (1)
	DMF		2.092	67	18 (1)
$[Cu(Ap4DM)]_2$	$CHCl_3$–py	1 : 2	2.083	79	14 (2)
	py		2.095	70	17 (1)
	DMSO		2.091	66.5	17.5 (1)
	DMSO–py	1 : 2	2.090	66	17.5 (1)
	DMF		2.091	68	17.5 (1)
	DMF–py	2 : 1	2.091	67.5	18 (1)
	DMF–py	1 : 1	2.089	66	18 (1)
	DMF–py	1 : 2	2.090	66	18 (1)
	DMF–py	1 : 5	2.086	78	14 (2)
	DMF–py	1 : 10	2.082	79	14 (2)
$[Cu(Appip)]_2$	$CHCl_3$		2.074	77.5	14 (1)
	$CHCl_3$–py	1 : 2	2.082	80	14 (2)
	py		2.092	72.5	17.5 (1)
	DMSO		2.096	67.5	18 (1)
	DMF		2.091	68	18 (1)
$[Cu(Sa3DH)]_2$[a]	py		2.096	73	(1)[b]
	DMF		2.094	73	(1)
	DMF–py		2.089	85	(2)
	DMSO		2.095	72	(1)
	DMSO–py		2.097	85	(2)
$[Cu(SA4Ph)]_2$[a]	py		2.097	73	(1)
	DMF		2.091	76	(1)
	DMF–py		2.088	82	(2)
	DMSO		2.097	72	(1)
	DMSO–py		2.094	85	(2)

[a] Reference 33.

[b] A(N) is not included for the various solutions, but reported to have a magnitude of 18 G.[33]

The uncomplexed thiosemicarbazones are significantly more active than their copper(II) complexes, and for most compounds there is little difference in the activity over the concentration range studied. The uncomplexed thiosemicarbazones retain their activity down to less than 20 $\mu g\ cm^{-3}$ against *Paecilomyces variotii*, but they and their copper(II) complexes show no activity against *Aspergillus niger*. H_2ApDE is the most active of the uncomplexed thiosemicarbazone and $[Cu(Ap4DE)]_2$ shows the greatest growth inhibition among the complexes. The trends in activity among the thiosemicarbazones (i.e. $H_2Ap4M < H_2Ap4E < H_2Ap4P$; $H_2Ap4M < H_2Ap4DE > H_2Ap4DP$; and $H_2Appip > H_2Aphexim$) are generally followed by their copper(II) complexes. This suggests that molecular size is important for biological activity, with H_2Ap4P, H_2Ap4DE and H_2Appip having the most appropriate size.

Supplmentary materials

Atomic coordinates have been deposited with the Director of the Cambridge Crystallographic Centre.

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Table 9. ESR spectral parameters of the copper(II) complexes of 2-hydroxyacetophenone thiosemicarbazones in different solvents at 77 K

Complex	Solvent	Cu : py	$g_{\parallel}$	$A_{\parallel}$ (G)	$g_{\perp}$	g_{av}
$[Cu(Ap4M)]_2$	$CHCl_3$		2.149	177	2.033	2.072
	$CHCl_3$–py	2 : 1	2.194	178	2.070	2.111
	$CHCl_3$–py	1 : 1	2.194	176	2.072	2.113
	$CHCl_3$–py	1 : 2	2.196	176	2.073	2.114
	py		2.186	176	2.064	2.105
	DMSO		2.208	175	2.083	2.125
	DMF		2.200	170	2.083	2.122
$[Cu(Ap4DM)]_2$	$Ni_2(Ap4DM)_2$		2.164	177	2.045	2.084
	$CHCl_3$–py	1 : 2	2.193	180	2.067	2.109
	py		2.188	176	2.066	2.107
	DMSO		2.186	177	2.062	2.103
	DMF		2.199	178	2.074	2.116
	DMF–py	2 : 1	2.184	180	2.059	2.102
	DMF–py	1 : 1	2.185	180	2.060	2.102
	DMF–py	1 : 2	2.182	182	2.056	2.098
	DMF–py	1 : 5	2.187	178	2.062	2.104
	DMF–py	1 : 10	2.192	173	2.071	2.111
$[Cu(Appip)]_2$	$CHCl_3$–py	1 : 2	2.182	188	2.053	2.096
	py		2.184	175	2.063	2.103
	DMSO		2.175	186	2.048	2.093
	DMF		2.195	180	2.036	2.089

Table 10. Activity of the 2-hydroxyacetophenone thiosemicarbazones and their metal complexes against *Paecilomyces variotii*

Compound	200[a]	400	600	1000	1600
H_2Ap4M	10.0[b]	20.2	21.0	22.5	22.7
H_2Ap4E	21.7	23.7	26.2	26.0	28.2
H_2Ap4P	23.5	26.0	28.0	27.3	28.7
H_2Ap4DM	11.3	17.7	20.2	20.5	21.8
H_2Ap4DE	39.8	40.8	40.7	41.0	40.3
H_2Ap4DP	23.2	23.2	24.3	25.0	25.0
H_2Appip	30.5	29.5	29.7	28.5	29.3
$H_2Aphexim$	23.5	26.5	27.8	27.3	26.6
$[Cu(Ap4M)]_2$	6.0	6.0	6.0	6.0	6.0
$[Cu(Ap4E)]_2$	17.8	9.2	9.0	10.2	10.0
$[Cu(Ap4P)]_2$	13.1	12.9	13.4	13.1	13.1
$[Cu(Ap4DM)]_2$	21.0	21.5	22.0	21.7	22.0
$[Cu(Ap4DE)]_2$	22.0	25.0	21.8	24.8	24.5
$[Cu(Ap4DP)]_2$	10.8	11.0	11.8	12.2	12.0
$[Cu(Appip)]_2$	19.3	19.0	19.0	20.4	19.9
$[Cu(Aphexim)]_2$	13.5	13.5	13.4	14.4	14.6

[a] mg cm^{-3}.
[b] mm diameter of growth inhibition zone (6.0 = no inhibition).

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