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Iron(III), Cobalt(II), Nickel(II), Copper(II) and Zinc(II) Complexes of 4-Formylantipyrine Thiosemicarbazone

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IRON(III), COBALT(II), NICKEL(II), COPPER(II) AND ZINC(II) COMPLEXES OF 4-FORMYLANTIPYRINE THIOSEMICARBAZONE

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ABSTRACT

Complexes of iron(III), cobalt(II), nickel(II), copper(II) and zinc(II) with 4-formylantipyrine thiosemicarbazone (HFoAtsc) have been prepared and spectrally and physically characterized. IR, electronic, and ESR spectra of the complexes, as well as IR, electronic and ¹H and ¹³C NMR spectra of HFoAtsc, have been obtained. The spectral studies show that HFoAtsc behaves as neutral or monobasic bidentate ligand in all complexes except [Fe(FoAtsc)_2]ClO₄ and [Co(HFoAtsc)_2](BF₄)₂, where the thiosemicarbazone bonds in a monobasic tridentate fashion in the former and a neutral tridentate manner in the latter. Coordination takes place via the azomethine nitrogen and the thione or thiolato sulfur for bidentate coordination and the carbonyl oxygen of the pyrazolone ring is added for tridentate coordination.

INTRODUCTION

Antipyrine (2,3-dimethyl-1-phenyl-5-pyrazalone) and its derivatives possess a wide variety of potentially useful biological properties.¹⁻⁵ Examples are antitumor³ and anti-inflammatory.⁵ Similarly, thiosemicarbazones have demonstrated significant biological activity and new examples continue to be tested for their antitumor and anti-HIV activity.^{6,7} Metal thiosemicarbazone complexes were found to be active against influenza,⁸ smallpox,⁹ protozoa¹⁰ and fungi.¹¹ The activity of thiosemicarbazones is thought to be due to their ability to strongly chelate traces of metal ions present in a biological system. There is also evidence that thiosemicarbazones inhibit the activity of ribonucleotide reductase, a necessary enzyme for the production of DNA,¹² as well as sever DNA strands.¹³ Here we report on the iron(III), cobalt(II), nickel(II), copper(II) and zinc(II) complexes of 4-formylantipyrine thiosemicarbazone (HFoAtsc), Figure 1.

RESULTS AND DISCUSSION

4-Formylantipyrine thiosemicarbazone was prepared by condensing 4-formylantipyrine (Aldrich) with thiosemicarbazide (Aldrich) in methanol with a few drops of concentrated sulfuric acid added to catalyze the reaction.

 H^+ C₁₁H₁₁N₂OC(H)=O + H₂NNHC(S)NH₂----->C₁₁H₁₁N₂OC(H)=NNHC(S)NH₂ MeOH, - H₂O

The stoichiometries of the isolated complexes of HFoAtsc are shown in Table I. Complexes of the neutral ligand are formed with tetrafluoroborates of cobalt(II) and nickel(II), copper(II) chloride and bromide, and zinc chloride. Complexes of the monobasic ligand are formed with iron(III) perchlorate; cobalt(II) chloride, bromide and acetate; nickel(II) chloride and bromide; and copper(II) acetate. In addition, two complexes, [Cu(HFoAtsc)(FoAtsc)](BF₄) and [Ni(HFoAtsc)(FoAtsc)(OAc)], are isolated with a combination of neutral and anionic ligands. Based on the stoichiometries shown in Table I, it appears that both the neutral and



E isomer

Figure. 1. Symbols and Numbering for 4-Formylantipyrine Thiosemicarbazone

anionic form of the ligand coordinate in a bidentate NS fashion. The carbonyl oxygen is not involved in coordination in any of the complexes except [Fe(FoAtsc)₂](ClO₄) and [Co(HFoAtsc)₂](BF₄)₂. The iron complex is yellow, cobalt complexes are brown, nickel and copper complexes are most often some shade of green and the zinc complex is white. Only the complexes prepared from tetrafluoroborates and perchlorate are electrolytes and the elevated molar conductivities found for some of the chloro and bromo complexes are due to partial decomposition of the complexes in solution. The iron(III) complex has a magnetic susceptibility value indicating high-spin octahedral stereochemistry. Among the cobalt complexes, only [Co(HFoAtsc)₂](BF₄)₂ has a normal magnetic susceptibility, while the other cobalt(II) complexes are binuclear and have values in the 0.7 - 1.6 B.M. range indicating significant interaction between cobalt centers, as well as the possibility of low-spin cobalt(II) centers. The nickel complexes [Ni(HFoAtsc)₂](BF₄)₂ and [Ni(HFoAtsc)(FoAtsc)(OAc)] have normal magnetic susceptibility values (ca. 2.8), while the other nickel complexes have lower values indicating spin-spin interaction between nickel atoms. The values for the mononuclear copper(II) complexes are near the theoretical value of 1.73 B.M., except for the binuclear [Cu(FoAtsc)(OAc)]₂.

TABLE I

Colors, Partial Elemental Analyses, Molar Conductivities and Magnetic Susceptibilities of the Complexes of HFoAtsc, C₁₃H₁₅N₅SO

Compound Empirical Formula	Color FW(Emp)	Found(Calc C	d %) H	N	۸ _M a	µ _{eff} b (B.M.)	dec. pt.(°C)
[Fe(FoAtsc)2]CIO4	yellow	42.3(42.7)	4.1(3.9)	19.0(19.1)	74.7	4.2	236 ^c
C ₂₆ H ₂₈ N ₁₀ O ₆ S ₂ CIFe	732.0						
[Co(FoAtsc)Cl]2	brown	41.1(40.8)	3.9(3.7)	18.6(18.3)	<10	0.7b	248
C13H14N5OSCoCI	382.7						
[Co(FoAtsc)Br]2	brown	36.8(36.6)	3.7(3.3)	16.2(16.4)	33.4	1.6 ^b	250
C ₁₃ H ₁₄ N ₅ OSCoBr	427. 2						
[Co(FoAtsc)(OAc)]2	dk. brown	44.2(44.3)	4.6(4.2)	17.2(17.2)	26.2	1.4 ^b	216
C ₁₅ H ₁₇ N ₅ O ₃ SCo	406.3						
[Co(HFoAtsc)2](BF4)2·3/2H2O	it. brown	37.0(37.3)	3.6(4.0)	16.8(16.7)	130	4.4	284
C52H66N20O7S4C02B4F16	1676						
[Ni(FoAtsc)Cl]2	lt. green	40.7(40.8)	3.9(3.7)	18.6(18.3)	42.2	1.5 ^b	264
C13H14N5OSNICI	382.5						
[Ni(FoAtsc)Br]2	lt. green	37.3(36.6)	3.9(3.3)	17.0(16.4)	37.4	1.6 ^b	282
C ₁₃ H ₁₄ N ₅ OSNiBr	426.9						
[Ni(HFoAtsc)(FoAtsc)(OAc)]- ·H ₂ O	yellow green	47.3(47.1)	4.8(4.8)	19.5(19.6)	<10	2.8	255
C ₂₈ H ₃₄ N ₁₀ O ₅ S ₂ Ni	713.5						
[Ni(HFoAtsc) ₂](BF ₄) ₂ ·H ₂ O	lt. green	37.2(37.6)	3.7(3.9)	16.6(16.9)	123	2.9	308
C ₂₆ H ₃₂ N ₁₀ O ₃ S ₂ NiB ₂ F ₈	829.0						
[Cu(HFoAtsc)Cl2]-1/2H2O	green	35.7(36.1)	3.2(3.7)	16.1(16.2)	17.1	1.8	260
C ₂₆ H ₃₂ N ₁₀ O ₃ S ₂ Cu ₂ Ol ₄	865.6						
[Cu(HFoAtsc)Br2] H2O	green	29.6(29.4)	2.8(3.2)	13.3(13.2)	52.2	1.8	252
C13H17N5O2SCuBr2	530.7	. ,		· · · · · · · · · · · · · · · · · · ·			
[Cu(FoAtsc)(OAc)]2	green	44.1(43.8)	3.9(4.2)	17.3(17.0)	38.0	0.9b	230
C ₁₅ H ₁₇ N ₅ O ₃ SCu	410.9						
[Cu(HFoAtsc)(FoAtsc)]BF4	lt. green	41.3(41.9)	3.6(4.2)	18.6(18.8)	63.8	1.7	218
C ₂₆ H ₂₉ N ₁₀ O ₂ S ₂ CuB ₂ F ₈	745. 8						
[Zn(HFoAtsc)Cl2]·H2O	white	35.0(35.2)	3.6(3.9)	15.9(15.8)	11.9	0	263
C13H17N5O2SZnCl2	443.7						

a)10⁻³ M in DMF and expressed as ohm⁻¹cm²mol⁻¹; b)per metal(II) center.

1H and 13C NMR Spectra

The ¹H NMR spectrum of HFoAtsc in d⁶-DMSO confirms its preparation and displays a resonance at $\delta = 13.109 (1 \text{ H})$, assignable to N(3)H involved in hydrogen bonding to the solvent. Also, this resonance is found in a similar position in the spectrum of the zinc complex ($\delta =$ 13.125). HFoAtsc possesses two N(4)H resonances at δ =7.885 and δ =7.918 indicating that these hydrogens are not involved in hydrogen bonding. These signals are shifted slightly to the downfield in the zinc complex and appear at δ = 7.918 and 8.022. Similarly, isatin thiosemicarbazone in DMSO has its N(3)H resonance at δ = 12.46 and the N(4)H₂ resonances at $\delta = 8.63$ and $9.01.^{14}$ However, the crystal structure results found for two isatin N(4)-substituted thiosemicarbazones^{14,15} indicate that in the solid state there is intramolecular hydrogen bonding between an N(4) hydrogen and N(1). This prompts us to suggest that HFoAtsc exists primarily as the E isomer in solution as depicted in Fig. 1. Compared to 4-formylantipyrine, the thiosemicarbazone has the resonance for H-C=N considerably upfield on replacing the oxygen by a nitrogen, but only small shifts occur for other hydrogens on conversion of the aldehyde into a thiosemicarbazone. The ¹³C assignments are consistent with the assignments of Koch.¹⁶ as well as assignments for N(4)-substituted thiosemicarbazones prepared from 2formylpyridine,¹⁷ 2-acetylpyridine,¹⁸ 2-benzoylpyridine,¹⁹ acetylpyrazine,²⁰ 2-hydroxyacetophenone,²¹ salicylaldehyde²² and isatin.¹⁴ The thiosemicarbazone molety's thione carbon is found at $\delta =$ 177 and the azomethine carbon at δ *ca*.150. We assign the resonance at δ ca. 161 to the carbonyl carbon which is in agreement with previous assignments for amide functions.14

IR Spectra

The most useful vibrational bands of HFoAtsc and its metal complexes for establishing the mode of coordination are reported in Table II. The hydrate water molecules have been omitted from Table II (and subsequent Tables) for convenience. It is known that the thione group, C=S, having an adjacent protonated nitrogen is relatively unstable and often changes over to the stable thiol form, C-SH, by enothiolization.²³

Downloaded by [Universitaets und Landesbibliothek] at 07:48 01 January 2014 Compounda v(N(4)H) v(CO) v(CN) v(CS) v(MN) v(MS) v(MX)3420s HFoAtsc 1630s 3240s 3380s [Fe(FoAtsc)2]ClO4 1625s 3260m 3380w [Co(FoAtsc)Cl]2 1630s 3260w 3430w [Co(FoAtsc)Br]2 1632s 3240w 3420w [Co(FoAtsc)(OAc)]₂ 1630s 3280w 3420s [Co(HFoAtsc)₂](BF₄)₂ 1625s 3318s 3400w [Ni(FoAtsc)Cl]2 3270w 3470m [Ni(FoAtsc)Br]2 3240m 3440w [Ni(HFoAtsc)(FoAtsc)-3280w (OAc)] 3420s [Ni(HFoAtsc)₂](BF₄)₂ 3320s 3350s [Cu(HFoAtsc)Cl₂] 3290w 3350m [Cu(HFoAtsc)Br₂] 3280w 3430w

TABLE II

Infrared Spectra (cm⁻¹) of HFoAtsc and its Metal Complexes

1590m 830s

1580w 736w

1572w 708s

1578w 735s

705s

704s

1572w

1570w

445w

445w

435w

445w

442w

345w

340w

330m

340m

330m

310w

320s

320m

705w 435m 340m 318w 1630s 1575s 1572m 708m 432w 1630s 340s 1632s 1585m 716m 430m 344m 1628s 1580m 738s 435w 330m 1630s 1580s 738s 448m 365w 1628s 1578m 734s 445w 340w [Cu(FoAtsc)(OAc)]₂ 1630s 1582m 715s 455m 345w 3300m 3415s [Cu(HFoAtsc)(FoAtsc)]-1628s 1577m 736s 450w 348w 3220m BF₄ 3440w [Zn(HFoAtsc)Cl₂] 1628s 1572s 742s 430m 335w 3260m

However, the absence of a v(SH) band in the spectrum of HFoAtsc, like the majority of thiosemicarbazones studied, 6,24 indicates that it is present in the thione form. The infrared spectrum of HFoAtsc shows a band at 1260 cm⁻¹ (not included in Table II), which may be assigned to a combination of v(C=S) and v(NCN).²⁵ The spectra of both HFoAtsc and its complexes show two absorption bands in the region 3220-3470 cm⁻¹ which may be assigned to $v_a(NH)$ and $v_s(NH)$, as well as v(OH) in the higher energy part of this region when hydrate water is present. Bands associated with coordinated water are absent in the spectra of the hydrates. The band at 1260 cm⁻¹ in the spectrum of HFoAtsc disappears in the spectra of some complexes (on deprotonation) due to change in the nature of NH-C(=S)-N to N=C(-S)-N on complexation.^{26,27} This is also supported by the appearance of a band at about 1610 cm⁻¹ characteristic of the new N=C group.⁶ The medium intensity, sharp band at 1590 cm⁻¹, assigned to v(C=N) in the spectrum of HFoAtsc, undergoes a shift to lower frequency (~ 15 cm⁻¹) in the complexes, consistent with coordination via the azomethine nitrogen, as is the presence of a band in the range 430-450 cm⁻¹ assignable to v(MN) for this nitrogen.²⁸ Coordination of the thione/thiol sulfur is indicated by a decrease in energy (i.e., 830 cm⁻¹ for HFoAtsc to ca. 735 cm⁻¹ for complexes with the neutral ligand and 705 cm⁻¹ for the anionic ligand in general) of the thioamide IV band, which derives considerable intensity from v(CS), as well as a band in the 330-370 cm⁻¹ range assignable to v(MS).²⁹ As is expected, greater decreases in the thioamide IV band occur for the anionic form of the ligand due to C-S formally becoming a single bond.⁶ The band at 1630 cm⁻¹ in the spectrum of HFoAtsc is assigned to v(C=O). Except for [Fe(FoAtsc)₂](ClO₄) and [Co(HFoAtsc)₂](BF₄)₂, which have this band shifted slightly to 1625 cm⁻¹, the spectra of the metal complexes show this band essentially unshifted, indicating non-involvement of the carbonyl function in coordination.

A band observed in the range 310-320 cm⁻¹ in the chloro complexes is assignable to the ν (MCl) mode,³⁰ but, unfortunately, our spectrometer does not allow assignment of ν (MBr). Extensive IR spectral studies reported on metal acetato complexes³¹ indicate that the acetato ligand may coordinate to a metal center in either a monodentate,

bidentate or bridging manner. The $\nu_a(\text{CO}_2$) and $\nu_s(\text{CO}_2)$ bands of the free acetate ions are at 1560 and 1416 cm⁻¹, respectively. In monodentate coordination v(C=O) is found at higher energy than $v_a(CO_2)$ and ν (C-O) is lower than ν_s (CO₂). As a result, the separation between the two v(CO) bands is much larger in monodentate complexes than the free ion, as found for [Ni(HFoAtsc)(FoAtsc)(OAc)] {*i.e.*, v_a(CO₂) = 1610 cm⁻¹, $v_s(CO_2) = 1305$ cm⁻¹ and v(Ni-O) = 410 cm⁻¹}. The opposite trend is observed in bidentate acetato coordination (no examples in this study); the separation between v(CO) is smaller than that of the free ion case. For bridging acetato with both oxygens coordinated as in copper(II) acetate, however, the two v(CO) bands are close to the free ion values³², as found for [Cu(FoAtsc)(OAc)]2 and [Co(FoAtsc)(OAc)]2 which have va at 1555 and 1530 cm⁻¹ with v_s at 1470 and 1415 cm⁻¹, respectively. The v(Cu-O) and v(Co-O) bands are assigned at 385 and 388 cm⁻¹. A broad band at ca. 1065 cm⁻¹ assignable to $v_3(BF_4)$ and a relatively sharp band at ca. 510 cm⁻¹ to $v_4(BF_4)$ indicate non-coordination of the tetrafluoroborate ions in each of their complexes, in agreement with the molar conductivity results, Table I. Also, the IR spectrum of the iron(III) complex shows a strong unsplit band (v_3) at *ca.* 1110 cm⁻¹ and a strong band at ca. 620 cm⁻¹, which are indicative of tetrahedral symmetry for the uncoordinated perchlorate ion.33

Solid State Electronic Spectra

Listed in Table III are the energies of the solid state electronic transitions for HFoAtsc and its complexes. Omitted from Table III are the higher energy $\pi \rightarrow \pi^*$ transitions (*ca.* 38000 cm⁻¹) which are not significantly altered on complex formation. The $n \rightarrow \pi^*$ transition associated with the azomethine portion of the thiosemicarbazone moiety is around 29000 cm⁻¹ in the spectrum of HFoAtsc and is generally shifted to higher energy on complexation (Table III). A second $n \rightarrow \pi^*$ band originating from the thioamide portion of the thiosemicarbazone moiety is found at somewhat lower energies. In the spectra of the complexes this latter band generally shifts to higher energies and sometimes merges with the $n \rightarrow \pi^*$ transition associated with the azomethine portion. Also present at energies below 30000 cm⁻¹ in the spectra of the metal ion

complexes are S \rightarrow M(II),M(III) charge transfer bands,³⁴ as well as Br \rightarrow M(II)³⁵ charge transfer bands. The Cl \rightarrow M(II)³⁶ and O \rightarrow M(II)³⁷ bands are generally found in the 30000 cm⁻¹ region of the spectrum and would be obscured by the stronger intraligand bands. This series of complexes has very broad bands due to the n $\rightarrow \pi^*$ transitions, and it is difficult to assign energies to the transition between 20000 and 30000 cm⁻¹. Similarly, it is difficult to assign energies of more than one d \rightarrow d band although energies for distinctive shoulders are assigned in Table III. The spectrum of the high spin iron complex [Fe(FoAtsc)₂]ClO₄ shows two bands at 20200 and 22120 cm⁻¹. These two bands are assigned to ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}$, but the lower value for the magnetic susceptibility, as well as the ESR spectra (*vide infra*), indicate that this solid may be a spin cross-over complex or a mixture of high and low spin iron(III) species. The bis(2-acetylpyridine N(4)-substituted thiosemicarbazone)iron(III) complexes were found to be low spin.³⁸

The spectrum of [Co(HFoAtsc)₂](BF₄)₂ is consistent with an approximately octahedral cobalt(II).39 The spectrum in the near-infrared region exhibits a broad band at 9090 cm⁻¹ assignable to v_1 of octahedral Co(II). The visible region of the spectrum has a strong band centered at 20700 cm⁻¹ with a shoulder at 18180 cm⁻¹ which may be due to v_2 . The main band is assigned to v_3 for octahedral Co(II), but calculation of v_2 shows this transition would be expected at 19390 cm⁻¹ (Table IV). Calculations of Dq, B and β based on this assignment yield 1121 cm⁻¹, 773 cm⁻¹ and 0.79, respectively. In low spin square planar cobalt(II) complexes, which appears to fit the remaining cobalt(II) complexes because of their low magnetic susceptibility values, seven spin-allowed d→d transitions are possible.40 The lowest energy bands in the 6900 cm⁻¹ region are assigned to a ${}^{2}A_{1g} \rightarrow {}^{2}E_{g}$ transition, the next highest to ${}^{2}A_{1g} \rightarrow {}^{2}B_{2g}$ (ca. 9500 cm⁻¹) and this energy is approximately 15B, the third to a transition to ²B_{1a} (usually weak and *ca.* 14000 cm⁻¹), the fourth to a transition to ²E'_a which is generally around 18000 cm⁻¹. The remainder of the transitions are at or above 20000 cm⁻¹ and are usually obscured by intraligand and charge transfer bands. For [Co(FoAtsc)Cl], [Co(FoAtsc)Br] and [Co(FoAtsc)OAc] approximate values of B are 635,

TABLE III

Solid State Electronic Spectra (cm⁻¹) of HFoAtsc and its Complexes.

Compound ^a	Intraligand and charge transfer	d→d
HFoAtsc	29850 24510	
[Fe(FoAtsc)2]ClO4	30490 25250	22120 20200
[Co(FoAtsc)Cl]2	28250 22030	18940 16830 13980 9520 6940
[Co(FoAtsc)Br] ₂	28250 24690	19760 15110 14220 9430 6890
[Co(FoAtsc)(OAc)] ₂	27780 22730	19610 17090 9710 6890
[Co(HFoAtsc) ₂](BF ₄) ₂	31250 25000	20700 18520 16130 9090
[Ni(FoAtsc)Cl] ₂	29940 22520	17610 16610 14080 10310 5160
[Ni(FoAtsc)Br]2	30120 23810	17240 14920 10050 5030
[Ni(HFoAtsc)(FoAtsc)- (OAc)]	27470 24390	17240 15920 10470
[Ni(HFoAtsc) ₂](BF ₄) ₂	30490 23040	17860 15380 14160 5235
[Cu(HFoAtsc)Cl ₂]	30120 24150	21270 14410
[Cu(HFoAtsc)Br ₂]	29150 24570	20490 14140
[Cu(FoAtsc)(OAc)] ₂	28810 23470	17480
[Cu(HFoAtsc)(FoAtsc)]- BF ₄	27780 23260	18870 14970 13600

TABLE IV

Assignments $(d \rightarrow d, cm^{-1})$ for the Cobalt(II) and Nickel(II) Complexes and their Ligand Field Parameters.

Complex ^a	⁴ T _{1g} → ⁴ T _{2g}	→ ⁴ A _{2g}	→ ⁴ T _{1g} (P)	Dq	В	β
[Co(HFoAtsc) ₂](BF ₄) ₂	9090	19390 ^b	20700	1027	856	0.88
	³ T1→ ³ T2	→ ³ A ₂	→ ³ T ₁ (P)			
[Ni(FoAtsc)Cl]2	4780 ^b	10310	14080	553	670	0.64
[Ni(FoAtsc)Br] ₂	4630 ^b	10050	14920	539	736	0.71
[Ni(HFoAtsc) ₂](BF ₄) ₂	4874 ^b	10470	14160	564	670	0.64

a)Hydrate waters omitted; b) calculated.

629 and 647 cm⁻¹, which is in the order expected based on the anionic, monodentate ligands.

The five-coordinate [Ni(HFoAtsc)(FoAtsc)(OAc)] shows d--> d spectral bands as follows: ${}^{3}B_{1} \rightarrow {}^{2}E_{,} 6800 \text{ cm}^{-1}$; ${}^{3}B_{1} \rightarrow {}^{2}B_{2}$, ${}^{3}A_{2}$, 10000 cm⁻¹; ${}^{3}B_{1} \rightarrow {}^{2}E_{,} 15290 \text{ cm}^{-1}$ and ${}^{3}B_{1} \rightarrow {}^{3}A_{2}$, ${}^{2}E(P)$, 17240 cm⁻¹. The magnetic susceptibility values for the remaining nickel complexes indicate a tetrahedral stereochemistry, rather than a square-planar one, and in Table IV the ligand field parameters have been calculated based on T_d symmetry.³⁶ Although the bromo complex, [Ni(Fotsc)Br]₂, has the lowest ligand field strength, it would not be expected to have the highest Racah parameter, B, and apparently be the least covalent. The two lowest energy bands around 14000 and 20000 cm⁻¹ for [Cu(HFoAtsc)Cl₂] and [Cu(HFoAtsc)Br₂] are in positions typically found for a square-planar configuration, and may be assigned to ${}^{2}B_{1g} \rightarrow {}^{2}A_{1g}$ and ${}^{2}B_{1g} \rightarrow {}^{2}E_{g}$, respectively.⁴¹

Solution Electronic Spectra

The solution spectra (DMSO) of 4-formylantipyrine thiosemicarbazone and its complexes are presented in Table V. A peak

TABLE V Solution (DMSO) Electronic Spectra (cm⁻¹) of HFoAtsc and its Metal Complexes

Compound ^a	Intraligand, C	d→d Bands		
HFoAtsc	29410(4.38)	27780		
[Fe(FoAtsc)2]ClO4	29410(4.68)	27250		18380(1.15)
[Co(FoAtsc)Cl] ₂	31650(4.50)	28900	27170	19920(2.88) 15150sh
[Co(FoAtsc)Br]2	29410(4.56)	27400	22830	19840(2.58)
[Co(FoAtsc)(OAc)]2	29760(4.49)	27320		19380(2.94)
[Co(HFoAtsc) ₂](BF ₄) ₂	30670(4.43)	27170		19460(1.94)
[Ni(FoAtsc)Cl]2	30390(4.51)	27770		16670(1.18)
[Ni(FoAtsc)Br]2	29760(4.52)	27470		16720(1.35)
[Ni(HFoAtsc)(FoAtsc)- OAc)]	29410(4.45)	28250		16890(1.90)
[Ni(HFoAtsc)2](BF4)2	30300(4.55)	27390		16610(1.69)
[Cu(HFoAtsc)Cl ₂]	29410(4.27)	27250	21930	14160(2.24)
[Cu(HFoAtsc)Br ₂]	28900(4.35)	27100		14450(2.21)
[Cu(FoAtsc)(OAc)] ₂	29070(4.48)	27170		16450(2.37)
[Cu(HFoAtsc)(FoAtsc)]- BF ₄	29760(4.63)	27390	19160	15020(2.16)

associated with the benzene $\pi \rightarrow \pi^*$ transition of the antipyrine molety is observed at about 38000 cm⁻¹ in the spectra of HFoAtsc and is nearly unshifted in the spectra of its metal complexes. A second band at ca. 29000 cm⁻¹, due to the $n \rightarrow \pi^*$ transition of the azomethine portion of the thiosemicarbazone molety, has a molar absorptivity, ε , of approximately 3 X 10⁴ (or log ε is ca. 4.4) for the coordinated and uncoordinated ligand. Although $CI \rightarrow M^{||}$ charge transfer bands might also be expected in this region of the spectrum, 36 it does not add significantly to the magnitude of ε in the various chloro complexes. A second $n \rightarrow \pi^*$ transition associated with the thione portion of the thiosemicarbazone moiety often appears as a low energy shoulder in the range of 24000-28000 cm⁻¹. In the complexes this band generally merges with the $n \rightarrow \pi^*$ transition of the azomethine portion of the thiosemicarbazone moiety and, therefore, bands in this region of the complexes are assignable to $S \rightarrow M(II)$, M(III)and other ligand $\{e.g., Br \rightarrow M(II), M(III)\}$ to metal charge transfer bands.³⁴ The solution $d \rightarrow d$ bands are altered from their energies in the solid state suggesting that significant interaction with DMSO molecules occurs.

ESR Spectra

Although a powder sample of [Fe(FoAtsc)₂]ClO4 failed to give a signal sufficiently more intense than the noise at high gain, we are able to determine g-values at 77K. High spin iron(III) commonly gives a broad isotropic peak, while low spin iron(III) is expected to have a anisotropic or rhombic spectrum with g_{\perp} (or g_1, g_2) > $g_{\parallel}(g_3) \approx 2$. The values in Table 6 indicate that the spectral parameters we have assigned are due to a low spin iron(III). In frozen DMF a well resolved spectrum (but shifted to lower magnetic field), which is consistent with low spin iron(III), 38 is observed.

The powder ESR parameters of the copper(II) complexes measured at room and liquid nitrogen temperatures are shown in Table VI. There is little alteration in the g-values of the powders at 298 K when cooled to 77 K indicating that there is no significant change in the axial interaction. The difference in the g_{II} values for the bromo and chloro complexes is due to the greater covalency of the former and has been noted before in heteronuclear thiosemicarbazone complexes.⁴² Comparing the g_{II} values of [Cu(HFoAtsc)Cl₂] and [Cu(FoAtsc)(OAc)]₂

Table Vi						
ESR Spectral Parameters of the Iron(III) and Copper(II) Complexes of HFoAtsc						
Compound ^a	Phase	Temp	g _{ll} or g ₁	g 2	g_{\perp} or g_3	gav or go
[Fe(FoAtsc)2]ClO4	solid	RT	а			
		77K	1.904		2.045	1.998
	DMF	77K	2.245	2.170	1.964	2.126
[Cu(HFoAtsc)Cl ₂]	solid	RT	2.203		2.048	2.100
		77K	2.199		2.047	2.098
	MeOH	RT		A₀=66G		2.109
[Cu(HFoAtsc)Br ₂]	solid	RT	2.183		2.046	2.092
		77K	2.180		2.043	2.089
	MeOH	RT		A₀=62G		2.103
[Cu(FoAtsc)(OAc)]2	solid	RT	2.186		2.043	2.091
		77K	2.183		2.040	2.088
	MeOH	RT		A ₀ =68G		2.091
	DMF	RT		A ₀ =78G		2.106
[Cu(HFoAtsc)(FoAtsc)]BF4	solid	RT	2.165		2.038	2.080
		77K	2.162		2.039	2.080
	MeOH	RT		A₀=67G		2.099
	DMF	RT		A ₀ =72G	A _N =13G	2.116

suggests that the latter is likely four-coordinate with acetato oxygen bridging. A lower g_{II} value of the complex [Cu(HFoAtsc)(FoAtsc)]BF₄ indicates more covalent, planar bonding due to the presence of two sulfur donors; the two ligands are likely bidentate N,S donors. The ESR spectra of MeOH solutions of all copper(II) complexes were recorded at room temperature. In solution a slight change from the powder g_{av} indicates an alteration in the coordination sphere (*i.e.*, for [Cu(HFoAtsc)Cl₂] powder $g_{av} = 2.100$ at RT and in MeOH solution $g_{av} = 2.109$ at RT). A shift to higher values in the spectrum of the solution compared to the powder spectrum is likely due to weak bonding of the solvent to the axial position of the planar copper(II) center. In DMF solution the two complexes [Cu(FoAtsc)(OAc)]₂ and [Cu(HFoAtsc)(FoAtsc)]BF₄ give even higher g₀ values than in MeOH indicating that DMF molecules coordinate to the metal center more strongly and may result in tetragonally-distorted sixcoordination.⁴²

The Racah parameters, k_{\parallel} and k_{\perp} , have values of 0.66, 0.77 and 0.62, 0.74 for [Cu(HFoAtsc)Cl₂] and [Cu(HFoAtsc)Br₂], respectively. The Racah parameter values show that there is considerable covalent nature²³ in the metal-ligand bonding for these complexes, and that inplane π -bonding is more important than out-of-plane π -bonding. However, a related complex prepared from a 4-formylantipyrine thiosemicarbazone in which N(4) is a part of a piperidine ring, [Cu(HFoAtscpip)Cl₂], had lower values of 0.55, 0.61 for k_{\parallel} and k_{\perp} , respectively. This illustrates that the nature of the thiosemicarbazone moiety has considerable effect on spectral properties and, very likely, biological properties, as has been shown by other classes of thiosemicarbazones.¹⁷⁻²²

In Figure 2 are the proposed structures for many of the compounds based on the physical and spectral evidence that is presented here. The compounds for which we have not specifically shown structures are the following: $[Co(HFoAtsc)_2](BF_4)_2$ is envisioned to be like the iron(III) species, but with neutral ligands; [Ni(HFoAtsc)(FoAtsc)(OAc)] is proposed to be close to square-pyramidal with the two thiosemicarbazone moieties bonding NS and the acetato ligand monodentate and $[Cu(HFoAtsc)(FoAtsc)]BF_4$ is thought to be four-coordinate with both



Figure 2. Proposed Structures for the Majority of the Complexes Prepared in this Study.

ligands bonding NS. To date no diffractable crystals have been grown, but we are hopeful that in the future we shall achieve crystals of complexes of the various types presented here.

EXPERIMENTAL

4-Formylantipyrine and thiosemicarbazide were purchased from Aldrich Chemical Company and used as received.

Preparation of HFoAtsc

4-Formylantipyrine (0.01 mol, 2.16 g) was dissolved in 50 mL of absolute EtOH and thiosemicarbazide was added portionwise followed by 3 drops of conc. H₂SO₄ and the mixture was refluxed for 2 hours. The resulting white solid was filtered, washed with cold isopropanol and then diethyl ether, and dried on a warm plate (35°C), yield = 2.54 g (87.9 %); mp = 217-9 °C.

Preparation of the Complexes

The metal complexes were prepared by refluxing a metal salt with HFoAtsc {1:1 (halides) and 1:2 (acetates, perchlorate and tetrafluoroborates) in anhydrous MeOH. The preparation of [Ni(FoAtsc)Cl]₂ is described as representative of the complexes in this report. An methanolic solution (15 mL) of anhydrous nickel chloride (0.448 g) was mixed with 15 mL of methanol containing (1.00 g of HFoAtsc). The mixture was refluxed for 2 h, cooled to room temperature, filtered with a scintered glass crucible with vacuum, washed with portions (3) of anhydrous ether to apparent dryness and stored in a desiccator until required for characterization. Yield: 1.26 g (95.7%). The yields were generally between 75 and 95 % for remaining complexes.

Physical Measurements

Partial elemental analyses were performed by National Chemical Consulting, Inc. of Tenafly, NJ. ¹H and ¹³C NMR spectra were recorded in d⁶-DMSO using a 300 MHz Varian NMR spectrometer. IR spectra were recorded as nujol mulls using a Perkin-Elmer 783 spectrometer. Solution (DMSO) and solid state (nujol mulls inpregnated into Whatcom # 1 filter paper) electronic spectra were acquired with a Perkin-Elmer 330 Spectrometer. Magnetic susceptibilities were determined with a Johnson-Matthey balance. ESR spectra were recorded with a Varian E104 Spectrometer in and calibrated with diphenylpicryl hydrazide.

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