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Thiosemicarbazones derived from 2,6-diacetylpyridine as tri- and pentadentate ligands of heavy metal ions

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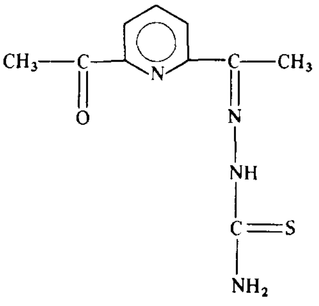
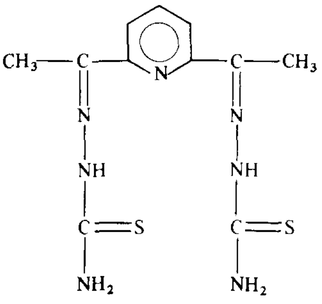
Abstract—The synthesis and elemental analysis of both 2,6-diacetylpyridine mono-thiosemicarbazone (**I**) and bis-thiosemicarbazone (**II**) are reported. Electronic and i.r. spectra of both reagents are described. **I** and **II** have two p*K* values: 1.27 ± 0.06; 11.30 ± 0.08 and 1.51 ± 0.02; 11.48 ± 0.09, respectively. The reactions of both reagents with Ni(II), Cu(II), Co(II) and Fe(III) were studied and discussed in order to test the ligating behaviour.

INTRODUCTION

The work described in this paper forms part of a systematic investigation of the use of thiosemicarbazones as ligands. The synthesis, properties and applications of two new compounds, 2,6-diacetylpyridine mono-thiosemicarbazone (DAPT) and 2,6-diacetylpyridine bis-thiosemicarbazone (DAPDT) are reported. The spectrophotometric reactions of Ni(II), Cu(II), Co(II) and Fe(III) with DAPT are compared with those of DAPDT. The nature of the metal chelates is also established.


DAPT


DAPDT

The behaviour of these reagents is noteworthy because the presence of a donor group in the α-position with respect to the thiosemicarbazide chain makes possible the formation of two five-membered chelate rings, whereas the introduction of another new thiosemicarbazide chain ensures up to five coordination sites, the formation of four five-membered chelate rings thus being possible. In both cases the chromogenic power of the reagents as well as the stability of chelates formed with metal ions increases [1]

EXPERIMENTAL

Synthesis of thiosemicarbazones

Both reagents were prepared as described elsewhere [1]. Analysis gave C 50.92, H 5.47, N 23.77 and S 13.82%; calculated for $C_{10}H_{12}N_4OS$: C 50.83, H 5.12, N 23.71 and S 13.57%. Found: C 41.86, H 4.79 and N 30.32%; calculated for $C_{11}H_{15}N_7S_2\frac{1}{2}H_2O$: C 41.50, H 4.71 and N 30.81%. DAPT and DAPDT decompose at 230 and 261°C, respectively.

Reagents

Both thiosemicarbazide derivatives are very soluble in dimethylformamide (solubility > 10 g l^{-1}). 0.1% (w/v) solutions of DAPT and DAPDT in this solvent were used. These solutions are stable for 1 week, at least under normal laboratory conditions, and for several months when stored in the dark at low temperature.

Standard metal ion solutions of 2.090 g Ni(II) l^{-1}, 1.000 g Cu(II) l^{-1}, 1.000 g Co(II) l^{-1}, 1.000 g Fe(III) l^{-1} were prepared from pure metals dissolved in nitric acid. Acetate (pH 4.7 or 5.9) and chloroacetate (pH 3.5) buffers were employed.

Apparatus

A Perkin–Elmer Coleman 575 spectrophotometer equipped with 1-cm glass or quartz cells was used. Infrared spectra of both reagents and Ni chelates were obtained in spectroscopically pure KBr discs and as Nujol mulls on a polyethylene plate with a Phillips SP 3–300 spectrometer. Thermogravimetric analysis of metal chelates were made with a Mettler TA-HE20 system with Pt/Pt-10%Rh thermocouples. A Metrohm 620 pH meter with glass–calomel electrodes and an AC/4 ATOM electrophoresis system, a cell with platinum electrode and ATOM 500 DC power supply for determining the charge on the metal chelates were also used.

RESULTS AND DISCUSSION

Infrared spectra

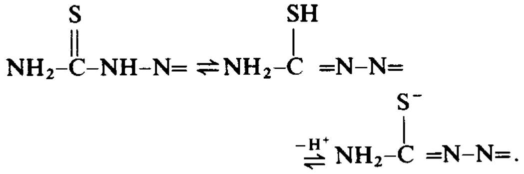
The assignments for the i.r. spectrum of pyridine are well established [2–4] as are those for thiosemicarbazide [5] and several thiosemicarbazones [5–8]. The principal bands and their assignments for DAPT, DAPDT, 2,6-diacetylpyridine (DAP) and thiosemicarbazide (T) are shown in Table 1. The well defined bands at about 3200–3400 cm^{-1} are characteristic of N–H stretching frequencies. Mono- and bis-derivatives primarily differ because the former shows the characteristic C=O stretching band.

Electronic spectra

DAPT (4.23×10^{-5} M) and DAPDT (3.23×10^{-5} M) solutions in dimethylformamide show absorption maxima at 323 nm ($\varepsilon = 2.2 \times 10^4$ l mol^{-1} cm^{-1}) and 330 nm ($\varepsilon = 4.3 \times 10^4$ l mol^{-1} cm^{-1}), respectively, as a consequence of the presence of the double thiosemicarbazide chain in the bis-derivative. Solution absorption spectra of DAPT show that increasing the polarity of the solvent (benzene, chloroform, 3-methyl-butan-1-ol, butan-1-ol, ethanol and methanol) causes a hypso- and hypochromic shift of the absorption maximum. We conclude that this band is probably due to an n–π^* transition [9].

Dissociation constants of the reagents

The absorption spectrum of DAPT shows an absorbance maximum at 305 nm in neutral or acidic aqueous solution (Fig. 1), but a red-shift occurs in basic solutions ($\lambda_{max} = 330$ nm). The case of DAPDT is similar (Fig. 1). This behaviour may be attributed to the deprotonation of the thiol group in the thiosemicarbazone molecule and to an increase in resonance of the π-system [10–12]:



$$NH_2{-}\overset{\overset{\displaystyle S}{\|}}{C}{-}NH{-}N{=} \rightleftharpoons NH_2{-}\overset{\overset{\displaystyle SH}{|}}{C}{=}N{-}N{=} \xrightleftharpoons{-H^+} NH_2{-}\overset{\overset{\displaystyle S^-}{|}}{C}{=}N{-}N{=}.$$

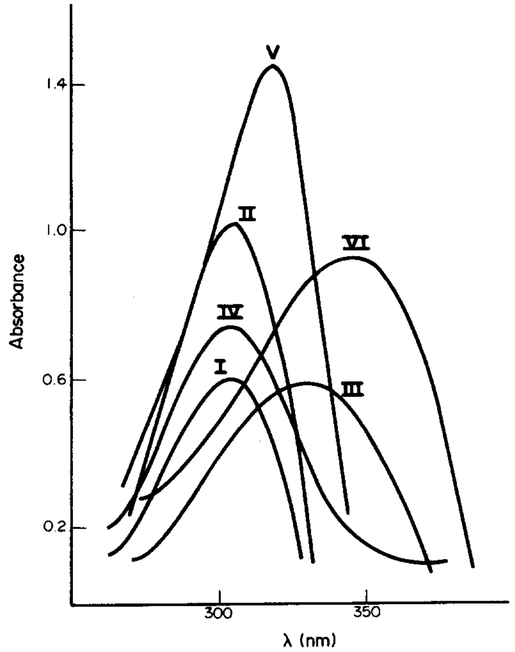


Fig. 1. Absorption spectrum of DAPT (I, pH 1.2; II, pH 5.4; III, pH 12.6) and DAPDT (IV, pH 1.3; V, pH 5.9; VI, pH 12.6) at 4.23×10^{-5} and 3.23×10^{-5} M, respectively.

The pK values were determined by the methods of PHILLIPS and MERRITT [13] and STENSTRÖM and GOLDSMITH [14]. Both reagents show two pK values: 1.27 ± 0.06 and 11.30 ± 0.08 for DAPT, and 1.51 ± 0.02 and 11.48 ± 0.09 for DAPDT. The first pK value is due to protonation of the pyridine nitrogen atom. This pK value is lower than in other related compounds, such as 2-acetylpyridine-4-phenyl-3-thiosemicarbazone [15] and phenyl-2-pyridyl-ketone-4-phenyl-3-thiosemicarbazone [16]: 4.31 and 3.80,

Table 1. Infrared spectrum of thiosemicarbazide derivatives (cm^{-1})

Assignment	DAPT	DAPDT	Ni-DAPDT	DPA	T
ν(NH)	3390 m 3260 m 3170 m	3400 m 3240 m 3190 m	3280 m		3380 w 3280 w 3190 w
ν(OH)				3380 w	
ν(=CH)	3090 vw 3015 vw	3130 w 3020 vw	3140 m	3080 w	
$\nu_{as}(CH_3)$	2940 vw	2980 vw		2975 w	
$\nu_{as}(CH_2)$				2925 w	
ν(N=C–S)			2180 vs		
ν(C=O)	1690 s			1690 s	
ν(C=C)				1650 sh	
$\delta(NH_2)$	1610 vs	1590 vs	1600 s		1610 s
Py	1590 w 1480 s	1495 s	1480 m	1580 w	
δ(NH)					1520 w
$\delta_{as}(CH_3)$	1440 s	1440 s	1430 m	1415 w	
$\delta_s(CH_3)$	1360 m	1370 w		1355 s	
ν(C=S)	1245 m 1170 w	1285 m 1150 w			1280 m 1160 m

Table 2. Photometric characteristics of metallic chelates

	DAPT				DAPDT			
	Ni(II)	Cu(II)	Co(II)	Fe(III)	Ni(II)	Cu(II)	Co(II)	Fe(III)
λ_{max} (nm)	370 (385)*	370 (385)	370 (410)	357 (430)	370 (385)	370 (410)	370 (415)	365 (425)
Optimum pH	5.5–6.3	3.0–6.0	4.5–6.0	3.2–4.0	5.0–6.0	4.0–5.5	5.2–6.6	4.0–5.5
Beer's law (ppm)	1–6	1–8	0.5–4.5	1–5	0.5–6.0	1–7	0.5–4.0	1–5
$\varepsilon \times 10^3$ ($l\,mol^{-1}\,cm^{-1}$)	8.53	6.08	10.68	6.69	9.22	7.46	11.4	8.74
Variation coefficient (%)	0.10	0.08	0.07	0.18	0.18	0.16	0.35	0.32
Metal/ligand ratio	1:2	1:1	1:2	1:2	1:1	1:1	1:1	1:1
Overall charge	Neutral	Positive	Positive	Positive	Neutral	Positive	Neutral	Positive

*The values in parentheses correspond to a shoulder in the absorption spectra.

respectively. The inductive effect of the $CH_3-\overset{\|}{C}-$ group and/or an intramolecular H bond between the iminic hydrogen and pyridinic nitrogen have to be involved to explain the low pK_1 values of both DAPT and DAPDT. The second pK value may be attributed to the deprotonation of the thiol group.

Effect of redox substances on absorption spectra

The presence of one or two C=S groups in the reagents suggests that instability might result from the oxidation of one or two of these groups. However oxidizing and reducing substances in moderate concentration (0.04% w/v) do not alter the electronic spectra of either DAPT or DAPDT.

Ligating characteristics of the thiosemicarbazones with transition metal ions

The chelate compounds (generally yellow or orange-yellow) are quickly formed. The metal complexes that exhibit highest absorptivity are Cu(II), Ni(II), Co(II) and Fe(III). Both thiosemicarbazide derivatives show a similar behaviour with those metals, detailed in Table 2. In general, DAPT and DAPDT form coloured complexes with transition metal ions at somewhat lower pH values than other related thiosemicarbazones [1]. This is probably because the protonation of the pyridine nitrogen atom lies at more acidic pH values in both DAPT and DAPDT than in other related compounds.

The oxidation state of the metals in these complexes was investigated. Reducing agents at pH 4.9 did not change the absorption spectra of the cobalt complexes. Oxygenated water produces a bathochromic shift on the absorption spectra of these complexes. These facts indicate an oxidation state for cobalt of two. In the same way, the oxidation states of iron and copper in their complexes of thiosemicarbazones were found to be three and two, respectively.

The data obtained on the stoichiometry (the continuous variation method was used) and the overall charge (Dowex 50 × 8 or 1 × 8, sodium or chloride forms, respectively, ion exchange resins were employed) of the metal complexes are summarized in Table 2. In general, the two reagents show different behaviour with respect to stoichiometric ratio in solution. However, there is no substantial difference in the chromogenic character of the reagents when they react with metal ions.

In order to compare possible coordination positions of both thiosemicarbazones, the nickel chelates were precipitated from aqueous medium in the optimal conditions of their formation. Neutral 1:1 Ni-DAPDT and Ni-DAPT precipitate with one and two water molecules, respectively. A strong band appears at 2180 cm^{-1} in their i.r. spectra that may be attributed to the N=C–S group stretching vibration [19]. The spectral region corresponding to the ν(NH) mode is more simple in the nickel chelates than in the free ligands. These facts suggest that the hydrogen atom of the $-\underset{\underset{S}{\|}}{C}-NH-$ group can split off producing a thiol group and participation of the thioenolate sulphur in coordination. This could explain the neutral character of the nickel-bis-thiosemicarbazone chelate. It is possible that DAPDT acts in this solid nickel complex as a "SNNS" tetradentate ligand [20]. On the other hand, the absence of the carbonyl group band in the i.r. spectrum of the Ni-DAPT chelate seems to indicate its enolization and participation in coordination. This could explain its neutral character; DAPT may act as an "ONS" tridentate ligand. DAPDT has two thiosemicarbazide chains and shows a potentially higher number of coordination positions than DAPT which has only a single thiosemicarbazide chain. However, the chromogenic power of the ligands is similar, as deduced from the data for metal chelates in solution.

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