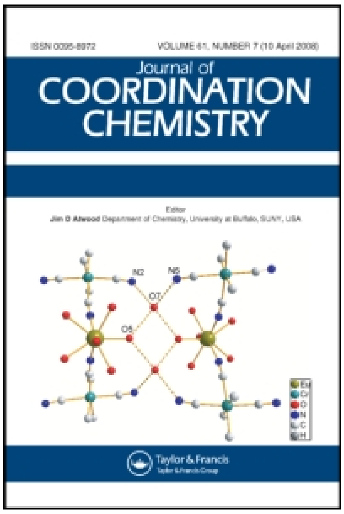

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METAL(II) COMPLEXES OF 1,1′-DIACETYLFERROCENE-BIS(4-PHENYLTHIOSEMICARBAZONE)

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A new ligand, 1,1′-diacetylferrocene-bis(4-phenylthiosemicarbazone) (H_2Dafpt) and some of its transition metal(II) complexes have been prepared. The complexes were characterized by elemental analyses, IR, NMR, electronic spectra, molar conductivities, magnetic moments and thermal analyses. Dafpt^{2-} coordinates to the metal ion with two thio-enol groups and acts as a tetradentate.

Keywords: Ferrocene, thiosemicarbazone, transition metals, complexes, synthesis

INTRODUCTION

Thiosemicarbazones are important due to their antibacterial,[1] anticarcinogenic and antifungal[2] properties. Transition metal complexes of thiosemicarbazones have also been screened for medicinal properties[3] and possess some degree of cytoxic activity.[4] In recent years, Omote and Bhagwansingh[5,6] have described some thiosemicarbazone ligands containing the ferrocenyl fragment and their complexes with Cu(II). In our laboratory, we have synthesized some new ferrocenyl thiosemicarbazones and their transition metal complexes.[7] In this paper, we extend this study to complexes of 1,1′-diacetylferrocene-bis(4-phenylthiosemicarbazone) (H_2Dafpt) with Cu(II), Ni(II), Zn(II), Co(II), Cd(II) and UO_2^{2+}.

EXPERIMENTAL

All solvents were dried using reported methods.[8] Hydrated metal acetates and other reagents were of analytical grade. 1,1′-Diacetylferrocene was obtained by literature methods.[9] 4-Phenylthiosemicarbazide was prepared according to a method described in the literature.[10]

H_2Dafpt was prepared by mixing 4-phenylthiosemicarbazide (0.06 mol) in absolute ethanol (50 cm^3) and 1,1′-diacetylferrocene (0.03 mol) in ethanol (30 cm^3). The reaction mixture was refluxed for 2 hrs, 1 cm^3 of glacial acetic acid was added and reflux continued for 2 hrs. The precipitate which formed was filtered and washed with hot ethanol and diethyl ether, then recrystallized from absolute ethanol. Yield 75%.

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Preparation of complexes

The complexes M(Dafpt).2–3H_2O (M = Cu(II), Ni(II), Zn(II), Co(II), Cd(II) and UO_2^{2+}), were prepared by the following method. H_2Dafpt (0.57g, 0.001 mol) was dissolved in anhydrous benzene (25 cm^3) by heating. The hot solution was filtered and added to the metal acetates (0.001 mol) in ethanol (25 cm^3). The resulting mixture was refluxed for 3 hrs. The product separated, was washed several times with water, warm ethanol and diethyl ether, then dried in a vacuum desiccator over anhydrous calcium chloride. Yield >75%.

Physical measurements

Microanalyses were carried out in the microanalytical laboratory of Lanzhou University. IR spectra were obtained with a Nicolet-10DX spectrophotometer using KBr discs in the 400–4000 cm^{-1} region. Electronic spectra (700–190 nm) in solution (DMF) as reference and corrected for) were recorded on a Perkin Elmer 240 spectrometer. ^1H NMR spectra were measured using an FT-80A spectrometer with $CDCl_3$ as solvent and TMS as internal standard. Conductivity measurements were performed using a DDS-12 conductometer and DMF as solvent at room temperature. DTA analyses were carried out with a DuPont 1090 thermal analyzer between room temperature and 900°C in a nitrogen atmosphere at a heating rate of 10°C/min. Magnetic measurements were made on a Gouy balance at room temperature using $(NH_4)_2SO_4.FeSO_4.6H_2O$ as calibrant.

RESULTS AND DISCUSSION

Analytical and physical data for the ligand and its complexes are listed in Table I. The data indicate that only complexes of thioenol form, M(Dafpt).nH_2O, were isolated. Formation of complexes may be represented by the following equation.

$$Fe(C_5H_4COCH_3)_2 + 2NH_2NHCSNHC_6H_5$$

$$\rightarrow Fe[C_5H_4C(CH_3){=}NNHCSNHC_6H_5]_2(H_2Dafpt) + 2H_2O$$

$$H_2Dafpt + M(OAc)_2.nH_2O \rightarrow M(Dafpt).nH_2O + 2HOAc$$

All complexes are insoluble in common solvents, but soluble in DMF and DMSO. In general, the thermal stability of the complexes is moderate; they decompose in the range 185–264°C. Values of molar conductivities, 2.13–5.82 $\Omega^{-1}\,cm^2\,mol^{-1}$, show that in DMF solution they are non-electrolytes.[11]

^1H NMR spectra

^1H NMR spectra of H_2Dafpt in $CDCl_3$ show that the eight protons on the substituted cyclopentadienyl rings is observed at 4.5 and 4.7 ppm as two singlets (8H). The signals for N^2H and N^4H appear at 9.3 (2H) and 8.9 ppm (2H), respectively. The signal at 7.3–7.7 ppm (multiplet) is due to phenyl ring protons (10H). CH_3 is observed at 2.3 ppm as a singlet (6H).

TABLE I
Analytical data for the ligand and its complexes.

	Formula	Yield (%)	Colour	M.P. (°C)	λm* (in DMF)	Analysis (calc. %) C	H	N
H_2DAfpt	$C_{28}H_{28}N_6S_2Fe$	75	yellow	143–145		59.27	4.97	14.75
						(59.15)	(4.96)	(14.79)
I	Cu(Dafpt).$2H_2O$	90	yellow-green	185	5.87	50.91	4.11	12.53
						(50.49)	(4.54)	(12.62)
II	Ni(DAfpt).$3H_2O$	92	reddish brown	220	3.04	49.92	4.31	12.66
						(49.51)	(4.75)	(12.38)
III	Zn(DAfpt).$2H_2O$	90	pale red	264	5.82	50.02	4.12	13.03
						(50.35)	(4.53)	(12.59)
IV	Co(DAfpt).$3H_2O$	85	brown	260	4.07	49.37	4.80	12.63
						(49.49)	(4.75)	(12.37)
V	Cd(DAfpt).$3H_2O$	88	pale yellow	214	2.13	45.50	4.52	11.97
						(45.88)	(4.40)	(11.47)
VI	UO_2(DAfpt).$2H_2O$	78	black	245	2.17	38.45	3.35	9.62
						(38.54)	(3.47)	(9.63)

* λm: molar conductance ($\Omega^{-1}\,cm^2\,mol^{-1}$).

^1H NMR spectra of the complexes Zn(Dafpt) and Cd(Dafpt) show that the signals at *ca* 9.3 ppm due to the protons on N^2H disappear. The signals of the protons attributed to N^4H, C_5H_4 and phenyl rings, and the methyl group appear at 8.85 (2H, br. s), 4.45 and 4.80 (8H, s) 7.3–7.7 (10H, m), and 2.4 ppm (6H, s), respectively. Thus the ligand coordinates in the enol form.

Infrared spectra

Principal absorption bands of the ligand and its complexes are listed in Table II. IR spectra of the H_2Dafpt show bands at 3294, 3120, 1586, 1278 and 780 cm^{-1} assignable to $\nu(N^4\text{—}H)$, $\nu(N^2\text{—}H)$, $\nu(C{=}N)$ and $\nu(C{=}S)$, respecyively. The bands observed at 1526, 1278, and 941 cm^{-1} are due to thioamide I-III modes,[12] *i.e.*, to $[\delta(C\text{—}H)+\delta(N\text{—}H)]$, $[\nu(C{=}S)+\nu(C\text{—}N)+\delta(C\text{—}H)]$ and $[\nu(C\text{—}N)+\nu(C{=}S)]$. Characteristic bands of ferrocene appear at 3080, 1441, 815 and 495 cm^{-1}.[13] In the complexes, M(Dafpt).nH_2O, $\nu(N^2\text{—}H)$ disappears and a new strong band, $\nu(C{=}N)^+$ is observed at *ca* 1590 cm^{-1}. The weak band at 780 cm^{-1} attributed to $\nu(C{=}S)$ is absent in the complexes, but a new band at about 590 cm^{-1} is observed, due to the C—S—M group, confirmed by a single band at 480 cm^{-1} assignable to $\nu(M\text{—}S)$.[14] The medium band at 1278 cm^{-1} also disappears because of the change N—C—N to N—C=N on complexing. Thioamide I shifts to lower wave numbers because of coordination of the nitrogen atom. The medium band at 1588 cm^{-1} registers a downfield shift (*ca* 30 cm^{-1}) in complexes, which indicates that the azomethine nitrogen coordinates to metal ions as well. The band at 1042 cm^{-1} due to $\nu(N\text{—}N)$ shifts to higher wavenumber (*ca* 13 cm^{-1}), providing further support. Water $\nu(O\text{—}H)$ appears at 3300–3400 cm^{-1} as a broad band.[15]

TABLE II
Characteristic IR and magnetic data for the ligand and its complexes (cm^{-1}).

	ν(N^2—H)	ν(N^2—H)	ν(C=N)	ν(C=N)$^+$	Thioamide I-IV	ν(N—N)	ν(C—S)	ν)M—S)	μ_{eff} (BM)
H_2Dafpt	3294m	3120m	1586m		1526s 1278m 941w 780w	1042m			
I	329m		1552m	1591s	1510s 892m	1056m	594w	474w	1.83
II	3298m		1556m	1595s	1510s 892m	1053m	596w	480w	diam.
III	3300m		1550m	1590m	1510s 892m	1056m	586w	482w	diam.
IV	3300		1555m	1591s	1510s 894m	1054m	584w	480w	3.78
V	3295m		1556m	1590s	1510s 896m	1054m	584w	480w	diam.
VI	3290m		1560m	1590s	1510s 893m	1054m	588w	481w	diam.

Electronic spectra

Magnetic moments are given in Table II. Electronic spectra (DMF) of the Cu(II) complex shows four bands at 15200, 20100, 22320 and 32100 cm^{-1}. Two low energy bands at 15200 and 20100 cm^{-1} are in positions typically found for a square-planar configuration, and may be assigned to $^2B_{1g}\rightarrow{}^2A_{1g}$ and $^2B_{1g}\rightarrow{}^2E_g$, respectively.[16,17] The high energy band at 32100 cm^{-1} is assigned to M→L charge transfer. That at 22300 cm^{-1} is attributed to charge transfer in the ferrocenyl group, and is close to that of the free ligand.[18] The magnetic moment (1.83 BM) for this complex is consistent with the proposed structure.

There are three bands in the electronic spectra of the Ni(II) complex at 17080, 20630 and 22400 cm^{-1}. The former two are assigned to $^1A_{1g}\rightarrow{}^1A_{2g}$ and $^1A_{1g}\rightarrow{}^1B_{1g}$ transitions, respectively, in a square-planar geometry.[19] Diamagnetic behaviour of the complex supports the proposed structure.

The electronic spectra of the Co(II) complex exhibit a very broad shoulder around 16700–19970 cm^{-1} and another band at 22430 cm^{-1}, suggesting a high-spin octahedral structure.[19] The band around 19970 cm^{-1} is due to the $^4T_{1g}(F)\rightarrow T_{1g}(P)$ transition and that at 16700 cm^{-1} may be assigned as $^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)$. The magnetic moment (3.78 BM) is consistent.

The UO_2^{2+} complex shows four bands at 34100, 31540, 22480 and 21340 cm^{-1}. That at 21340 cm^{-1} may be assigned to the $^1E_g\rightarrow 3\pi_4$ transition of the uranyl group.[20] Other bands observed at 31540 and 34100 cm^{-1} are assigned to H_2Dafpt→O=U=O charge transfer.

Thermal analysis

Thermal analyses results for the ligand and its complex Cd(Dafpt).3H_2O are listed in Table III. It is seen that the ligand melts endothermally at 144.5°C without weight

TABLE III
Thermal analyses data for the ligand and Cd(Dafpt).3H_2O.

	D.T. (°C)	Corresponding mass	Weight loss[a]
H_2Dafpt	143–145 (m.p.)	2C_6H_5SH	39.6
	182.6–335.4		(38.8)
	335.4–496.2	2C=N	9.0
			(9.2)
	496.2–650.7	2C_5H_4+2C(CH_3)=NNH	43.1
			(42.3)
	up to 860	residual, Fe	10.7
			(9.8)
Cd(Dafpt).3H_2O	62.8–174.3	3H_3O	8.0
			(7.4)
	235.4–365.4	2C_6H_5NH	(24.8
			(25.1)
	365.4–395.8	2CH_3	3.6
			(4.1)
	395.8–651.8	2C_5H_4+2C=NN=C—S	39.7
			(40.4)
	up to 860	residual, Fe and Cd	23.0
			(23.0)

[a] Calculated values are given in parentheses.

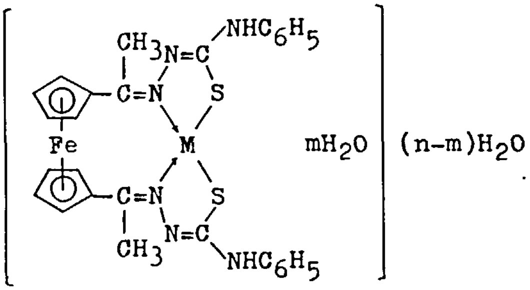

FIGURE 1 Suggested structural arrangement for the complexes: M = Cu, Ni and Zn, m = 0; M = Cd, Co and UO_2^{2+}, m = 2.

loss, then decomposes exothermally at 182.6–335.4°C, losing about 39.6% of its weight. C=N groups decompose at 335–496°C. Decomposition of (Cd(Dafpt).3H_2O is different to the ligand; it loses about 8.0% weight at 63–174°C, corresponding to the loss of one molecule of lattice water and two molecules of coordinate water. Ligand decomposition occurs in two ranges, 235–265°C and 365–396°C. The complexes are more stable than the ligand, thermally.

H_2Dafpt acts as a tetradentate ligand, coordinating to the metal ion in the thio-enol form. Plausible structures for the complexes are shown in Figure 1.

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