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Synthesis, Spectral and Magnetic Investigation of 4-(2pyridyl)-1-salicylaldehyde-3thiosemicarbazone

Usama El-Ayaan $^{\rm a}$, Gaber Abu El-Reash $^{\rm a}$, Peter Weinberger $^{\rm b}$ & Wolfgang Linert $^{\rm b}$

^a Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt

^b Institute of Inorganic Chemistry, Vienna University of Technology, Getreidemarkt-9, A-1060, Vienna, Austria

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SYNTHESIS, SPECTRAL AND MAGNETIC INVESTIGATION OF 4-(2-PYRIDYL)-1- SALICYLALDEHYDE-3-THIOSEMICARBAZONE

Usama El-Ayaan^a, Gaber Abu El-Reash^a, Peter Weinberger^b and Wolfgang Linert^{*,b}

^a Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt ^bInstitute of Inorganic Chemistry, Vienna University of Technology, Getreidemarkt-9, A-1060 Vienna, Austria e-mail: wlinert@mail.zserv.tuwien.ac.at

ABSTRACT

Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Pd(II) and dioxouranium(VI), $(UO_2^{2^+})$, complexes of 4-(2-pyridyl)-1-salicyldehyde-3-thiosemicarbazone (H₂SBT) have been synthesized and characterised by elemental analyses, molar conductance, spectral (IR, visible and NMR) and magnetic moment measurement. IR spectral data show that the ligand behaves in a bi-, tri- and/or tetradentate manner. An octahedral structure is proposed for Cr(HSBT)₂Cl.H₂O, Mn(HSBT)₂, Fe(HSBT)Cl₂ · H₂O, Ni(SBT) · 2H₂O and Co(HSBT)₂Cl · H₂O, while a square-planar structure is found for Ni(H₂SBT)₂Cl₂ · 2H₂O. Pd(HSBT)₂, Cu₃(HSBT)₂Cl₄ · 2H₂O and Cu₂(SBT)(OAc)₂ · 2H₂O.

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Fig. 1. Structure of the Ligand (H₂SBT).

INTRODUCTION

Sulphur compounds containing NS and NSO donor $atoms^{1-3}$ and their 3d-metal complexes have been found to exhibit fungicidal, bactericidal, antiviral and antitubercular activities. Studies on metal complexes of 2-hydroxybenzaldehyde-3-thiosemicarbazone^{4,5} or 2-hydroxybenzaldehyde-4-substituted-3-thiosemicarbazone have been reported. In this paper we report the preparation and characterisation of some new metal complexes derived from 4-(2-pyridyl)-1-salicyldchyde-3-thiosemicarbazone (H₂SBT) (Fig. 1) with some transition metals.

EXPERIMENTAL

Preparation of the Ligand

4 (2-Pyridyl)-3-thiosemicarbazide was synthesized according to the general literature method⁶. The ligand was prepared by boiling an ethanolic solution of 4(2-pyridyl)-3-thiosemicarbazide with salicylaldehyde under reflux for about 1 h. The yellow crystals of H₂SBT (m.p. 193 °C) were removed by filtration, washed with ethanol and recrystallized from hot ethanol.

Preparation of 4-(2-Pyridyl)-3-thiosemicarbazide. 4-(2-Pyridyl)-3thiosemicarbazide was synthesized in three steps according to the general literature method⁶ as follows: *Firstly: Preparation of Triethylammonium N-2-Pyridyldithiocarbamate.* 2-Amino-pyridine (0.2 mol,19 g), carbon disulphide (0.2 mmol,15.2 mg) and triethylamine (0.33 mmol,33 mg) were warmed to give a clear solution. Two phases separated rapidly and the whole mixture was shaken at room temperature for 24 h, when the

contents solidified. The product was filtered and then washed with ether and air-dried. The lemon-yellow plates formed were triethylammonium N-2-pyridyldithiocarbamate, m.p. 85 °C, yield 49.0 g (90.5 %).

Secondly: Preparation of Methyl-2-pyridyldithiocarbamate. Methanol (100 mL) was added to triethylammonium N-2-pyridyldithiocarbamate (0.14 mg, 0.5 mmol), followed by methyl iodide (30 mL, 0.5 mmol). After 1 h, water was added into the solution and pale yellow needles of methyl-2-pyridyldithiocarbamate were formed, m.p. 101 °C, yield 75.6 g (76 %).

Thirdly: Preparation of 4(2-Pyridyl)-3-thiosemicarbazide. A mixture of 0.005 mol (0.93 g) of methyl-2-pyridyldithiocarbamate and 0.5 mL (0.01 mmol) of hydrazine hydrate in 2 mL of absolute ethanol was heated for 5 minutes. An abundant amount of crystalline precipitate of 4-(2-pyridyl)-3-thiosemicarbazide was formed, m.p. 193 °C, yield 55 g (97 %).

Preparation of the Metal Complexes

All complexes were prepared by refluxing equimolar quantities (2 mmol) of H₂SBT and the hydrated metal salts (chloride or acetate) in ethanol (100 mL) or aqueous ethanol (ethanol to water 3:1) for 2-6 h. Mn(HSBT)₂ was precipitated after addition of sodium acetate as buffering agent. The resulting solid complexes were filtered while hot, washed with ethanol followed by diethyl ether and dried *in vacuo* over CaCl₂.

RESULTS AND DISCUSSION

The analytical and physical data for the metal complexes are listed in Table I. The isolated solid complexes are quite stable in air and insoluble in common organic solvents, but soluble in DMF and DMSO. The molar conductivities were $1 \times 10^{-3} \Omega^{-1} \text{cm}^2 \text{mo}\Gamma^1$ in DMSO solution at 25 °C, indicating the non-electrolytic nature of all of the complexes, except for Cu₃(HSBT)₂Cl₄ · 2H₂O which shows a value corresponding to a bis-univalent electrolyte in DMSO.

NMR Spectra of the Ligand (H₂SBT)

The NMR spectrum of H₂SBT in DMSO-d₆ shows three signals at $\delta = 10.6$, 11.5 and 12.8 ppm relative to TMS which disappear upon adding D₂O and can be assigned to

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TABLE 1. Analytical and Physical Data for the Complexes Derived from H₂SBT

		1		0,1	1 1 / 1 /		1000 100	
Compound	Colour	ו שים		Found (C	alcd.) %		A _m (DMSO)	yield
Empirical formula, (F. Wt)		(°C)	W	cı	c	H	Ω^{-1} cm ² mol ⁻¹	%
Cd(HSBT)OAc	greenish	>300	25.4		40.9	3.3	4	16
C ₁₅ H ₁₅ CdN ₄ O ₅ S (443.4)	yellow		(25.4)		(40.8)	(3.2)		
Cd(HSBT)CI	yellow	275	27.0	8.6	37.1	2.70	17	85
C ₁₃ H ₁₁ CdCIN ₄ OS (418.9)			(26.9)	(8.5)	(37.3)	(2.65)		
Co(HSBT) ₂ Cl · H ₂ O	brown	241	8.9	5.4	47.5	3.5	37	87
C26H24CICoN8O3S2 (654.5)			(0.0)	(5.4)	(47.7)	(3.7)		
Co(SBT) 3H ₂ O	brown	>300	15.3	,	40.9	4.1	П	<u> 06</u>
C13H16C0N4O4S (383.0)			(15.4)		(40.8)	(4.2)		
Cr(HSBT) ₂ Cl · H ₂ O	brown	>300	8.0	5.4	48.1	3.7	41	92
C ₂₆ H ₂₄ ClCrN ₄ O ₃ S ₂ (647.5)			(8.0)	(5.5)	(48.3)	(3.7)		
Cu ₂ (SBT)(OAc) ₂ · 2H ₂ O	yellowish	228	23.2		37.2	3.8	5	06
C17H20CU2N4O7S (551.0)	green		(23.0)		(37.1)	(3.7)		
Cu ₃ (HSBT) ₂ CL 2H ₂ O	yellowish	200	21.1	15.5	34.5	2.8	65	86
C26H26CLCu3N6O4S2 (910.5)	green		(21.0)	(15.6)	(34.3)	(2.9)		
Fe(HSBT)Cl ₂ ·H ₂ O	brown	274	13.3	17.2	37.4	3.1	48	88
C ₁₃ H ₁₃ Cl ₂ FeN ₄ O ₂ S (415.8)			(13.4)	(17.1)	(37.6)	(3.2)		
Hg(H ₂ SBT) ₂ Cl ₂	yellow	265	24.4	80.00 80.00	•	,	29	68
C ₂₆ H ₂₄ Cl ₂ HgN ₈ O ₂ S ₂ (815.6)			(24.6)	(8.7)				
Mn(HSBT) ₂	yellowish	>300	9.1		52.3	3.8	37	92
C ₂₆ H ₂₁ MnN ₆ O ₂ S ₂ (597.0)	brown		(9.2)		(52.4)	(3.7)		
Ni(H ₂ SBT) ₂ Cl ₂ · 2H ₂ O	pale brown	243	13.7	16.1	35.9	3.7	37	95
C13H16Cl2N4NiO2S (421.7)			(13.4)	(16.2)	(35.7)	(3.7)		
Ni(SBT) · 2H ₂ O	yellowish	>300	15.9	,	42.7	3.8	6	88
C ₁₃ H ₁₄ N ₄ NiO ₂ S (348.7)) brown		(16.1)		(42.9)	(3.9)		
Pd(HSBT) ₂	yellowish	>300	16.3	r	48.1	3.6	9	16
C ₂₆ H ₂₂ N ₈ O ₂ PdS ₂ (674.4) brown		(16.4)		(48.3)	(3.4)		
$UO_2(SBT) + H_2O$	red	>300	42.5		28.2	2.4	9	94
C ₁₃ H ₁₂ N ₄ O ₄ SU (558.0	6		(42.7)		(28.0)	(2.2)		
Zn(HSBT)Cl · H ₂ O	yellow	258	16.6	9.3	40.0	3.5	6	92
CuHuCINOSZn (389.5			(16.8)	(1.1)	(40.1)	(3.4)		
Zn(SBT) - H ₂ O	yellow	>300	18.3	·	44.4	3.6		06
C ₁₃ H ₁₂ N ₄ O ₂ SZn (353. ⁴	4)		(18.5)		(44.3)	(3.4)		

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NH (2), NH (4) and OH protons, respectively. The multiplet at 6.9-8.4 is assigned to phenyl ring protons.

IR Spectra of the Ligand (H₂SBT)

The principal IR bands of H₂SBT are listed in Table II. The IR spectrum of H₂SBT (in KBr) shows three bands at 1620, 1615 and 1600 cm⁻¹ while are assigned to v(C=N) (azomethine), v(C=C) phenyl and [v(C=C) and v(C=N)] of the pyridyl ring, respectively⁷. The bands located at 1480, 1270, 910 and 775 cm⁻¹ assigned to thioamide I-IV vibrations⁸ have substantial contributions from v(C-N), δ (C-H), δ (N-H) and v(C-S) vibrations. The bands at 3110 and 3050 cm⁻¹ are assigned to v(N-H) (4), v(N-H) (2), respectively. The presence of v(O-H) as a broad band at lower wavenumber (3280 cm⁻¹) and the weak bands in the 1860-1980 and 2000-2180 cm⁻¹ regions suggest intramolecular hydrogen bonding (OH----N) as shown in Fig. 1. The possibility of thione/thiole tautomerism (HN-C=S/N=C-SH) is ruled out, since no band characteristic for a thiole group (2500-2650 cm⁻¹) is found in the spectrum of the ligand. The band observed at 1385 is due to δ (OH)⁹.

IR Spectra of the Complexes

H₂SBT behaves as a neutral bidentate ligand coordinating through the nitrogen of the azomethine group and the thione sulphur atom. This behaviour which is found in Hg(H₂SBT)₂Cl₂ and Ni(H₂SBT)₂Cl₂ · 2H₂O (Fig. 2), is revealed by (i) the shift of ν (C=N) to higher wavenumbers and the clear change in both intensity and position of the thioamide IV bands and (ii) the position of the bands assigned to δ (OH), ν (NH) and ν (C-O) remaining practically unchanged, indicating that NH and OH groups of the ligand are not involved in bonding.

In Fe(HSBT)Cl₂ · H₂O, Cu₃(HSBT)₂Cl₄ · 2H₂O, Cd(HSBT)Ac and Cd(HSBT)Cl, H₂SBT acts as a uninegative tridentate ligand, coordinating *via* the deprotonated OH, NH and the sulphur atom of the thione group. This mode of complexation is confirmed by (i) the disappearance of δ (OH) and the shift of *v*(NH) to higher wavenumbers and *v*(CS) to lower wavenumbers. The insolubility of Cu₃(HSBT)₂Cl₄ · 2H₂O in most

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TABLE II. IR Spectral Bands of H₂SBT and its Metal Complexes (only the Most Intense Bands are Shown).

Compound	v(CN) ⁴	v(CN) ^b	v(CS)	v(S-C=N)	v(C-S)	v(N-H)	ð(OHI)
Cd(HSBT)Cl	1640 vs	1600 sh	765 s			3120 m	-
Cd(HSBT)OAc	1630 vs	1585 s	770 s	ı		3110 m	•
Co(HSBT)2CI · H2O	1655 vs	1600 s	,	1580 s	700 w	,	1390 s
Co(SBT) · 3H2O	1635 vs	1600 sh		1570 s	м 069		
Cr(HSBT) ₂ Cl · H ₂ O	1650 vs	1600 s		1580 s	700 w		1385 s
$Cu_2(SBT)(Ac)_2 \cdot 2H_2O$	1630 vs	1615 sh		1570 s	700 w	•	·
Cu ₃ (HSBT) ₂ Cl ₄ -2H ₂ O	1655 vs	1600 s	770 s	,	•	3100 m	,
Fe(HSBT)Cl ₂ · H ₂ O	1640 vs	1600 s	760 s	•		3120 m	
H ₂ SBT	1620 vs	1600 sh	775 s			3110 m	1350 m
Hg(H ₂ SBT) ₂ Cl ₂	1645 vs	1604 s	765 s		•	3120 m	1385 s
Mn(HSBT)2	1660 vs	1610 s	,	1560 s	700 w		1390 s
Ni(H ₂ SBT) ₂ Cl ₂ · 2H ₂ O	1655 vs	1600 s	760 s	•		3110 m	1390 s
Ni(SBT) - 2H ₂ O	1640 vs	1615 s	,	1580 s	650 w	·	
Pd(HSBT) ₂	1640 vs	1600 s	,	1540 s	685 w		1390 s
$UO_2(SBT) \cdot H_2O$	1660 vs	1600 s		1560 s	700 w	ı	
Zn(HSBT)Cl · H ₂ O	1655 vs	1600 s	,	1580 s	680 w	•	1390 s
$Zn(SBT) \cdot H_2O$	1640 vs	1600 s		1580 s	680 w	ı	
azomethine ^b pyridine							

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Fig. 2. The Suggested Structure of the Ni(H₂SBT)₂Cl₂ · 2H₂O Complex



Fig. 3. The Suggested Structures of Cu₃(HSBT)₂Cl₄ · 2H₂O

polar and non-polar organic solvents suggests its polymeric nature. Two structures [(I) and (II) in Fig. 3] may be suggested.

The observed room-temperature magnetic moment of 1.66 B.M. excludes structure (I), since this type of bridging arrangement should cause a lowering in the magnetic moment values¹⁰ as a result of the commonly found strong antiferromagnetic interaction. The high shift of v(C-O) suggest the presence of a bridging phenolic C-O

group¹¹. The colour change to yellow after addition of pyridine confirmed the presence of a chlorine bridge. The molar conductance value of 65 Ω^{-1} cm²mol⁻¹ in DMSO, although somewhat low for a bivalent electrolyte in this solvent, supports structure (II). Therefore, structure (II) containing a four-coordinated square-planar structure with both oxygen and chlorine bridging would be consistent with the magnetic and spectral data.

In Cr(HSBT)₂Cl · H₂O, Co(HSBT)₂Cl · H₂O, Zn(HSBT)Cl · H₂O and Pd(HSBT)₂, HSBT⁻ behave as a mononegative bidentate ligand in the thiol form, coordinating *via* the deprotonated SH and CN (azomethine) groups as shown in Fig. 4. This behaviour is confirmed by the following evidence: (i) the absence of v(NH) and the thioamide IV v(CS) bands, (ii) the shift of both v(C=N) and v(N-N) to higher wavenumbers, (iii) the appearance of new bands assigned to v(S-C=N) and v(C-S) and (iv) the presence of δ (OH), v(C-O) and [v(C=C) + v(CN)] of the pyridine ring at the same position of the ligand suggesting that the OH and the nitrogen of the pyridine ring points out of the coordination sphere.

In Mn(HSBT)₂, HSBT⁻ behaves as a mononegative tridentate ligand in the thiol form, coordinating *via* the deprotonated SH, C=N (azomethine) and the nitrogen of the pyridine ring. The presence of v(OH) at 3410 cm⁻¹ as a sharp band and δ (OH) at 1390 cm⁻¹ confirmed that the OH group does not coordinate to the metal ion. The absence of v(NH) and thioamide IV v(CS) bands confirmed the deprotonation of SH and the shift of [v(C=C) + v(CN)] of the pyridine ring to higher wavenumbers, suggesting the participation of the pyridine nitrogen in the coordination sphere.

In Co(SBT) \cdot 3H₂O, Zn(SBT) \cdot H₂O, and UO₂(SBT) \cdot H₂O, SBT² behaves as a binegative tridentate ligand coordinating *via* the deprotonated OH group, C=N (azomethine) and the deprotonated CS group in the thiol form. This behaviour is revealed from (i) the disappearance of v(NH), v(OH) and v(CS) bands, (ii) the shift of v(C=N), v(C-O) and v(N-N) to higher wavenumbers and (iii) the appearance of new bands assigned to v(S-C=N) and v(C-S) frequencies. The absence of signals due to



Fig. 4. The Suggested Structure of the Cr(HSBT)₂Cl · H₂O Complex

acetate protons in the NMR spectrum of the zinc and uranyl complexes confirmed the tridentate behaviour of SBT²⁻.

Also, in $Cu_2(SBT)(Ac)_2 \cdot 2H_2O$ and Ni(SBT) $\cdot 2H_2O$, H_2SBT acts as binegative tetradentate ligand *via* the deprotonation of both OH and thiol C-S groups, and the C=N of azomethine and pyridine nitrogen. The low shift of v(CO) suggests the absence of bridging phenolic C-O groups¹¹. The insolubility of these complexes in suitable non-polar solvents did not allow molecular weight measurements. Geometrical factors prevent the coordination of all donors to a single metal ion, which must, in this case, act as a bridging unit between two metal centres giving a dimeric structure as shown in Fig. 5¹².

The uranyl complex exhibits three bands at 910, 810 and 260 cm⁻¹, assigned to v_3 , v_1 and v_4 vibrations, respectively, in the dioxouranium ion¹³. The force constant (F) for the bonding sites of v(U=O) is calculated by the method of McGlynn *et al*¹⁴; the F_{UO} value is 6.84 dynes Å⁻¹.

New bands observed in all complexes at 580-520, 485-450, 380-320 and 320-270 cm⁻¹ are tentatively assigned to the $v(M-O)^{15}$, $v(M-N)^{16}$, $v(M-S)^{15}$ and $v(M-Cl)^{17}$, respectively.

Electronic Spectra and Magnetic Moments

The band positions, magnetic moments and calculated ligand field parameters are given



Fig. 5. The Suggested Structures of Cu₂(SBT)(OAc)₂ · 2H₂O and Ni(SBT) · 2H₂O Complexes

in Table III. The molar extinction coefficients are all within the range of 100 confirming they are d-d transitions.

The electronic spectrum (DMSO) of Cr(HSBT)₂Cl · H₂O shows several bands in the regions 16,400-17,540 (v₁) and 20,500-23,260 (v₂) cm⁻¹. We could not observe the expected v₃ band on our instrument which might be hidden under v₂. The three spinallowed transitions for chromium(III) in an octahedral field are as follows: ${}^{4}A_{2g}$ (F) $\rightarrow {}^{4}T_{2g}$ (F) (v₁), ${}^{4}A_{2g}$ (F) $\rightarrow {}^{4}T_{1g}$ (F) (v₂) and ${}^{4}A_{2g}$ (F) $\rightarrow {}^{4}T_{1g}$ (P) (v₃). The v₁ transition is a direct measurement of the ligand field parameter 10Dq. From v₁ and v₂, the value of B and β may be calculated. In addition, the μ_{eff} -value may be taken as additional evidence for the octahedral geometry.

The electronic spectrum of the Mn(HSBT)₂ complex in DMSO shows three bands at 14,370, 16,950 and 24,160 cm⁻¹ assignable to ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}$, ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}(G)$ and ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}(D)$ transitions¹⁵, respectively. The calculated B, β and Dq values lie in the same range as reported for octahedrally coordinated Mn(II) ion^{18,19}. On increasing delocalisation, β decreases and becomes less than unity in the complex.

The diamagnetic nature of $Co(HSBT)_2Cl \cdot H_2O$ indicates that it is a cobalt(III) rather than a cobalt(II) complex. This observation is in keeping with the finding of other

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TABLE III. Magnetic Moments, Electronic Bands and Ligand Field Parameters of the Complexes Derived from H₂SBT (Molar Extinctions are Around 100 Confirming they are d-d Transitions; Solvent Used: DMSO).

		Relative Molar				
Compound	Band position cm ⁻¹	Extinction Coefficients at 16400 cm ⁻¹	Dq	£	đ	μ _{eff} (B.M.)
Co(HSBT) ₂ Cl · H ₂ O	15340, 22730	25	2392	598	0.56	diam.
Co(SBT) · 3H ₂ O	13090, 14280, 22700, 24750	11	825	1260	1.3	3.4
Cr(HSBT)2CI · H2O	16400, 17540, 20500, 21740	100	1639	698.5	0.76	3.9
	23260, 31250					
$Cu_2(SBT)(OAc)_2\cdot 2H_2O$	16890, 24040	45	ł	ı		1.50
Cu ₃ (HSBT) ₂ Cl ₄ · 2H ₂ O	16130, 24100	43	ŀ	,		1.63
Fe(HSBT)Cl ₁ · H ₂ O						6.1
Mn(HSBT);	14370, 16950, 24155	0.06	658.6	599	0.62	5.9
Ni(H ₂ SBT) ₂ Cl ₂ · 2H ₂ O	22990, 26050	100		·	•	diam.
Ni(SBT) · 2H ₂ O	23580, 26315	·	•	,		2.6
Pd(HSBT) ₂	23580, 27625	63	,			diam.
UO ₂ (SBT) · H ₂ O	18520, 24155	·	I	,	ı	diam.

workers that ligands with thiol groups generally oxidise cobalt(II) ions to produce cobalt(III) complexes. The spectrum of this complex in DMSO displays two bands at 15,340 and 22,730 cm⁻¹ assignable to ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ and ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ transitions of octahedral geometry. The value of B, β and Dq are typical for low-spin octahedral cobalt(III)²⁰. The magnetic moment value (3.4 B.M.) for Co(SBT) \cdot 3H₂O is near the spin-only value of 3.8 B.M. for high-spin octahedral cobalt(II) complexes²¹. The spectrum (in DMSO) shows two peaks around 13,090-14,300 and 22,700-25,400 cm⁻¹ assignable to ${}^{4}T_{1g} \rightarrow {}^{4}A_{2g}(v_2)$ and ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)(v_3)$ transitions. The values of the ligand field parameters are consistent with the octahedral geometry of cobalt(II).

The Ni(H₂SBT)₂Cl₂ · 2H₂O complex was found to be diamagnetic which suggests a square-planar, four-coordinated structure. The spectrum of this complex in DMSO shows a band at 22,990 cm⁻¹ (v₂) which may be assigned to ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$ and another band around 26,050 cm⁻¹ (v₂) which may be assigned to a spin-forbidden transition. The fact that no band is observed below 10,000 cm⁻¹ indicates a square-planar stereochemistry for these complexes²⁰. Square-planar nickel(II) complexes with sulphur ligands generally exhibit an additional well-defined band around 11,000 cm⁻¹ referred to as v₁, but in the present complex this band is absent. The magnetic moment value (2.6 B.M.) for Ni(SBT) · 2H₂O is consistent with octahedral geometry of the Ni(II). The spectrum of this complex shows one strong band at 23,590 cm⁻¹ (v₃) assignable to the ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}(P)$ transition. The other characteristic bands for d-d transitions are difficult to be recognized in this complex and thus the ligand field parameters cannot be calculated.

The diamagnetic nature of Pd(HSBT)₂ indicates a square-planar geometry, as expected for d⁸ metal ions²². Further, the electronic spectrum shows a band at 23,580 cm⁻¹ due to the ${}^{1}A_{1g} \rightarrow {}^{1}B_{1g}$ transition suggesting planar configuration²³.

The spectra of the Cu(II) complexes show an asymmetric broad band at approx. 16,800 cm⁻¹ which is assigned to the ${}^{2}T_{2g} \rightarrow {}^{2}E_{g}$ transition; the band position is in agreement with those generally observed for square-planar copper(II) complexes²⁴.

THIOSEMICARBAZONES

The low magnetic moment of the copper acetate complex (2 B.M.) supports a dimeric or polymeric structure.

Dioxouranium(VI) compounds with the equatorial coordination number four absorb below 20,000 cm⁻¹, while compounds with more than four equatorial groups do not^{25,26}. The UO₂(SBT) · H₂O complex shows two bands in its spectrum, the first is at 24,160 cm⁻¹ which definitely can be assigned to the ${}^{1}\Sigma_{8}^{-} \rightarrow {}^{2}\pi_{4}$ transition of dioxouranium(VI)²⁵, and the second at 18,520 cm⁻¹ indicates an equatorial number of four.

Conclusions

Core S, N donation is augmented by the phenolate oxygen donor to the harder metals, particularly Fe(III) and Cu(II) (the case of Cd(II) goes against the anticipated trend). Cd(II) is harder than Hg(II), leading to N,S coordination. The behavior of Cr(III) compared to Fe(III) suggests that the slower kinetics of Cr(III) substitution is what leaves a pendant phenol rather than a coordinated phenolate. Evidence is cited for pyridine coordination for the Mn(II) complex. The d^5 Fe(III) chose the phenolate donor; the d^5 Mn(II) chose the pyridyl in agreement with the softer Mn(II) center compared to Fe(III). The Ni(II) in a strong field (N, S) also does not need either phenolate nor pyridyl as axial ligands; it is square-planar. This is repeated for Pd(II), as anticipated.

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