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## Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsrt19

# Synthesis and Equilibrium Studies of the Metal Complexes of 4-Amino-N-(2,6-dimethyl-4-pyrimidinyl)benzenesulfonamide (Sulphadimidine)

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To cite this article: Wafaa M. Hosny (1997) Synthesis and Equilibrium Studies of the Metal Complexes of 4-Amino-N-(2,6-dimethyl-4-pyrimidinyl)-benzenesulfonamide (Sulphadimidine), Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 27:2, 197-220, DOI: <u>10.1080/00945719708000146</u>

To link to this article: http://dx.doi.org/10.1080/00945719708000146

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## SYNTHESIS AND EQUILIBRIUM STUDIES OF THE METAL COMPLEXES OF 4-AMINO-N-(2,6-DIMETHYL-4-PYRIMIDINYL)-BENZENESULFONAMIDE (SULPHADIMIDINE)

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#### ABSTRACT

The formation equilibria of the complexes of some transition metal ions with sulphadimidine (SDD) have been investigated by a potentiometric technique. The stepwise formation constants of the complexes formed in solution were calculated using the non-linear least-squares computer program MINIQUAD. The concentration distribution of the complex species was determined. Complexes of Cu(II), Cr(III), Ni(II), Co(II), Zn(II), Hg(II), Cd(II), UO<sub>2</sub>(VI) and Pd(II) have been synthesized and characterized by elemental analyses, electrolytic conductance, electronic, IR, <sup>1</sup>H NMR, and mass spectra and thermogravimetric studies. The ligand forms 1:1 complexes (metal ion : ligand) with Cu(II), Zn(II), Hg(II), Cd(II), UO<sub>2</sub>(VI) and Pd(II) and 1:2 complexes with Cr(III), Ni(II) and Co(II).

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## **INTRODUCTION**

Sulphadimidine has been used in the treatment of meningococcal meningitis and vibrio cholerae, as well as some staphylococci and streptococci. Much work has been done determining sulphadimidine (SDD) in livestock products<sup>1</sup>, edible animal tissues<sup>2</sup> and in milk. In the present paper we report the synthesis and the determination of the stability constants of Cu(II), Cr(III), Ni(II), Co(II), Zn(II), Hg(II), Cd(II), UO<sub>2</sub>(VI) and Pd(II) chelates with SDD using potentiometric The of the synthesized metal chelates were technique. structures physico-chemical established by techniques, including spectral, conductance, magnetic measurements and thermogravemetric studies.

## **EXPERIMENTAL**

#### **Materials**

Solutions of Cu(II), Cr(III), Ni(II), Co(II), Zn(II), Hg(II), Cd(II), UO<sub>2</sub>(VI) and Pd(II) were prepared from the following analytical grade salts: copper(II) chloride, chromium(III) chloride, nickel(II) chloride, cobalt(II) chloride, zinc(II) chloride, mercuric(II) chloride, cadmium(II) chloride and potassium tetrachloropalladate(II), respectively. All solutions were standardized by standard procedures<sup>4</sup>. Sulphadimidine (SDD) was obtained from E. Merck, and was used without further purification. A SDD solution (250 mL, 0.01 M) was prepared immediately before use by dissolving in an equivalent amount of (25 mL, 0.10 M) HNO<sub>3</sub>. Carbonate-free NaOH (titrant) was prepared and standardized against potassium hydrogen phthalate solution.



Fig. 1. Structure of SDD.

## Synthesis of Metal Complexes

The Cu(II), Zn(II), Hg(II), Cd(II), UO<sub>2</sub>(VI) and Pd(II) complexes with SDD were prepared in the ratio of 1:1 (metal ion : ligand), while the Cr(III), Ni(II) and Co(II) complexes with SDD were prepared in the ratio of 1:2. A quantity of 0.556 g of SDD dissolved in aqueous sodium hydroxide solution (10 mL, 0.20 M) was mixed with the corresponding equivalent amount of the metal salt dissolved in 5 mL water. Immediately, insoluble coloured solids of the complexes precipitated, which were recrystallized in N,N-dimethylformamide. After 2 weaks the microcrystalline powders of these complexes were collected by filtration, washed with water, ethanol and finally dried in air. All these complexes were characterized by elemental analyses and mass spectra (Table 1). The complexes are soluble in organic solvents ( $Et_2O$ , CHCl<sub>3</sub>, acetone and DMSO) and insoluble in H<sub>2</sub>O.

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Complex	Mass (molecular lon) m/z (calc.)	Colour	%	Dec. Point °C	U	Н	Z	W	CI	ohm <sup>-1</sup> .cm <sup>2</sup> .mol <sup>-1</sup>	μeff. B.M.
1. CuLCI.H <sub>2</sub> 0 [C <sub>12</sub> H <sub>15</sub> N <sub>4</sub> 0 <sub>3</sub> SCICu]	393 (394)	brown	80	>220	36.5 (36.5)	3.7 (3.8)	14.2 (14.2)	16.1 (16.1)	9.2 (9.0)	11.0	1.8
2. [CrL <sub>2.</sub> 2H <sub>2</sub> 0]Cl [C <sub>24</sub> H <sub>30</sub> N <sub>8</sub> 0 <sub>6</sub> S <sub>2</sub> ClCr]	676 (677.5)	pale green	85	>210	42.6 (42.5)	4.4 (4.6)	12.4 (12.5)	7.9 (7.7)	5.2 (5.2)	69.7	3.6
<sup>3.</sup> NiL <sub>2</sub> .2H <sub>2</sub> O [C <sub>24</sub> H <sub>30</sub> N <sub>8</sub> O <sub>6</sub> S <sub>2</sub> Ni]	645 (648.7)	pale green	06	>216	44.6 (44.4)	4.6 (4.6)	17.4 (17.3)	9.2 (9.0)		5.7	3.4
4. CoL <sub>2.2</sub> H <sub>2</sub> O [C <sub>24</sub> H <sub>30</sub> N <sub>8</sub> O <sub>6</sub> S <sub>2</sub> Co]	646 (648.9)	violet	06	>218	44.3 (44.4)	4.4 (4.6)	17.4 (17.3)	9.2 (9.1)	1	8.5	4.9
5. ZnLCI.H <sub>2</sub> O [C <sub>12</sub> H <sub>15</sub> N <sub>4</sub> O <sub>3</sub> SCIZn]	394 (395.9)	white	80	>200	36.5 (36.4)	3.6 (3.8)	14.2 (14.1)	16.5 (16.5)	9.2 (9.0)	5.9	dia.
6. HgLCI.H <sub>2</sub> 0 [C <sub>12</sub> H <sub>15</sub> N <sub>4</sub> 0 <sub>3</sub> SCIHg]	530 (531.1)	white	75	>192	27.0 (27.1)	2.6 (2.8)	10.6 (10.5)	37.8 (37.8)	6.9 (6.7)	6.4	dia.
7. CdLCI.H <sub>2</sub> O [C <sub>12</sub> H <sub>15</sub> N <sub>4</sub> O <sub>3</sub> SCICd]	440 (442.9)	white	80	>224	32.6 (32.5)	3.3 (3.4)	12.4 (12.6)	25.4 (25.4)	8.2 (8.0)	7.5	dia.

Table I. Analytical Data and Physical Properties of the SDD<sup>a</sup> Complexes.

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8. U02LCI.H20 [C <sub>12</sub> H <sub>15</sub> N505SCIU]	600 (600.9)	pale yellow	82	>227	24.2 (24.0)	2.3 (2.5)	9.5 (9.3)	39.5 (39.7)	6.0 (5.9)	12.2	dia.
9. PdLCI.H <sub>2</sub> O [C <sub>12</sub> H <sub>15</sub> N <sub>4</sub> O <sub>3</sub> SCIPd]	434 (439.9)	dark red	85	>211	33.3 (33.0)	3.3 (3.4)	12.6 (12.8)	25.5 (24.5)	8.3 (8.1)	9.6	dia.

a SDD = LH

## **Potentiometric Titrations**

Potentiometric measurements were made using a Metrohm 686 titroprocessor (Switzerland) equipped with a 665 Dosimat. The electrode and titroprocessor were calibrated with standard buffer solutions prepared according to NBS specifications<sup>5</sup>. The pH meter readings (B) recorded in EtOH-H<sub>2</sub>O solution were converted to hydrogen concentration [H<sup>+</sup>] by means of the following widely used relation<sup>6</sup>.

$$-\log[H^+] = B + \log U_H \tag{1}$$

where  $\log U_{\rm H}$  is the correction factor for the solvent composition and ionic strength  $\mu$  for which B is read. The value of  $\log U_{\rm H}$  at the ionic strength 0.1 M and 25±0.1°C, was found to be -0.20.

## Procedure and Technique

The following mixtures were prepared and titrated potentiometrically against a NaOH solution (0.0964 M) for the determination of both the acid dissociation constants of SDD was determined by titrating mixture (A), and the stability constants of the metal ion complexes with SDD were determined by titrating mixture (B). All titrations were performed in a purified N<sub>2</sub> atmosphere:

(A) 0.01 M SDD (10 mL) + 0.4 M KNO<sub>3</sub> (10 mL) + 20 mL ethanol.

(B) 0.01 M SDD (10 mL) + 0.01 M metal ion solution (5 mL) + 0.8 M
 KNO<sub>3</sub> (5 mL) + 20 mL ethanol.

The mixture (C) was titrated conductometrically against 0.0964 M NaOH.

## (C) 0.01 M SDD (10 mL) + 0.01 M metal ion solution (10 mL) + 20 mL ethanol.

The equilibrium constants were evaluated from titration data. These are defined by eqs (2) and (3).

$$p(M) + q(L) + r(H)$$
 (M) $_{p}(L)_{q}(H)_{r}$  (2)

$$\beta_{pqr} = \frac{[(M)_{p}(L)_{q}(H)_{r}]}{[M]^{p}[L]^{q}[H]^{r}}$$
(3)

Where M, L, H stand for the metal ion, ligand and proton, respectively. The calculations were performed using the computer program<sup>8</sup> MINIQUAD-75 and were conducted on an IBM computer. The model selected was that which gave the best statistical fit and proved consistent chemically with the titration data without giving any systematic bias in residuals. The calculations were restricted to data obtained at pH values below 9 or before precipitation in order to avoid complications due to the hydrolysis of complex species at higher pH. The results obtained are shown in Table II.

## **Physical Measurements**

The electrolytic conductance was measured by means of a WTW conductivity bridge, model LBR. IR spectra were recorded as KBr pellets on a Perkin-Elmer 1430 spectrophotometer. Electronic spectra were taken by a Shimadzu UV-160 A spectrophotometer. The NMR spectra were obtained using a Varian Gemini 200 spectrometer (200 MHz). Dimethylsulphoxide (DMSO) was used as a solvent. Mass spectra were recorded on a Hewlett-Packard model MS-5988. The mass spectra were carried out at 220°C and 70 eV. The magnetic susceptibilities of the solid complexes were measured at room temperature by the Gouy

Complex	р	q	r*	logβÞ	υc	Sď
S D D	0 0	1 1	1 2	8.67(0.01) 11.45(0.02)	52	3.8E-9
CuLCI.H <sub>2</sub> O	1	1	0	4.97(0.02)	48	3.8E-6
{CrL <sub>2</sub> .2H <sub>2</sub> 0}CI	1	1	0	4.72(0.09)	48	7.8E-6
NiL <sub>2</sub> .2H <sub>2</sub> O	I	1	0	3.90(0.10)	50	6.4E-6
CoL <sub>2</sub> .2H <sub>2</sub> O	1	1	0	3.57(0.08)	42	7.1E-7
ZnLCI.H <sub>2</sub> O	1	1	0	3,11(0.09)	47	9.4E-6
HgLCI.H <sub>2</sub> O	1	1	0	3.24(0.06)	51	3.5E-7
CdLC1.H <sub>2</sub> O	1	1	0	3.06(0.10)	42	3.9E-6
UO2LCI.H20	1	1	0	5.43(0.11)	47	5.2E-6
PdLC1.H <sub>2</sub> O	1	1	0	5.01(0.09)	56	3.1E-7

Table II. Formation Constants of the Metal Complexes of SDD.

 ${}^{a}$ p, q and r are the stoichiometric coefficients corresponding to metal ion, ligand and H<sup>+</sup>, respectively; <sup>b</sup>Standard deviations are given in parentheses; <sup>c</sup>Number of data points; <sup>d</sup>Sum of square of residuals. method using a magnetic, Johnson Matthey Alfa Products, UK, model MKI, susceptibility balance. The calibrating compound used was  $[Hg(CoCNS)_4]$ . Diamagnetic corrections were calculated from Pascal's constants<sup>7</sup>. The water content of the complexes was determined gravimetrically by using a modern, computerized Perkin-Elmer TGA 7 system, with a scanning rate of 20°C min<sup>-1</sup>.

## **RESULTS AND DISCUSSION**

Suphadimidine (SDD) in acid medium behaves as a diprotic acid  $[H_2L]^+$  according to the following equilibria.



Since the heterocyclic nitrogen is more basic than the amino nitrogen, the conjugate acid of the studied ligand HL is expected to have the form  $[H_2L]^+$ . Such an acid will have two possible dissociation constants, namely  $pK_{a_1}$  and  $pK_{a_2}$  corresponding to the two equilibria (4) and (5) respectively. The average values of the  $pK_a$ 's computed this way were found to be 2.78 and 8.67. They were reproducible to  $\pm 0.01$ . The value of 8.67 for  $pK_{a_2}$  is similar to that reported for benzaldehyde-N-benzenesulfonylhydrazine<sup>9</sup> and that of N-benzene sulfonylbenzamide<sup>10</sup> ( $pK_a = 8.22$ ). The potentiometric titration curves of the Cu(II)-SDD system taken as a representative are presented in Fig. 2. The titration curve of SDD starts at pH = 3 and passes through a low-buffer pH-region, followed by an inflection due to neutralization of the <sup>+</sup>NH group. Above pH = 8, the curve results in another buffer region due to the neutralization of the NH group and formation of complex. The potentiometric curve of the Cu(II)-SDD complex is lower than the SDD titration curve. This indicates that the Cu(II)-SDD complex is formed through the release of a hydrogen ion. The model fitted, according to the method of calculation described above, is found to consist of the 1:1 species,  $[Cu(L)]^+$ .

The stoichiometries and stability constants of the complexes formed were determined by trying various possible composition models for the system studied. The model selected was that which gave the best statistical fit and which was chemically consistent with the titration data without giving any systematic drifts in the magnitudes of various residuals. Table II lists the equilibrium constants together with their standard deviations and the sum of the square of residuals as obtained from the program MINIQUAD-75.

The results show that the stability of the metal chelates follows the order Co<Ni<Cr<Cu>Zn. This order is in good agreement with that found by Mellor and Naley<sup>11</sup> and by Irving and Williams<sup>12</sup> for 3d transition metal ions. The classic sharp maximum for the Cu(II) complex is due to the stabilizing contribution of the Jahn-Teller effect. With respect to increasing electronegativity of the metals, the electronegativity difference between metal atom and donor atom of the ligand will decrease, hence the metal-ligand bond would have more covalent character which may result in greater stability of the metal chelates.



Fig. 2. Potentiometric Titration Curves of the Cu(II)-SDD System. (A) SDD; (B) 1:1 Cu(II):SDD

Plotting  $\log K_1$  values against electronegativities of the metal atoms<sup>11</sup> gives more or less a straight line as shown in Fig. 3.

The conductometric titration curves of the SDD complexes, taking the Cu(II)-SDD complex as a representative example are given in Fig.4. These show an initial decrease in conductance and an inflection at a =1.04. This probably corresponds to the neutralization of NH resulting from the formation of the [Cu(L)]<sup>+</sup> complex. In the 2.08 > a > 1.04 range, the conductance slightly decreases due to the neutralization of <sup>+</sup>NH. Beyond a = 2.08, the conductance increases appreciably due to the presence of an excess of NaOH.

The concentration distribution of various species formed in solution (formation %) as a function of pH provides a useful picture of metal ion binding towards the ligand. The distribution curve of the Cu(II)-SDD system, taken as a representative, is shown in Fig. 5. Under the prevailing experimental conditions, the extent of complex formation was found to be pH dependent.

## **Characterization of Metal Complexes**

The reaction involved in the preparation of the metal complexes of the ligand SDD (HL) may be represented according to the following equations

$$M^{2+}+L^{+}+Cl^{+}+H_{2}O$$
  $\longrightarrow$  MLCl.H<sub>2</sub>O (M = Cu, Zn, Hg, Cd, UO<sub>2</sub> or Pd) (6)

$$M^{3+}+2L^{2}+Cl^{2}+2H_{2}O$$
 [ML,  $2H_{2}O$ ]Cl (M = Cr) (7)

$$M^{2^+} + 2L^- + 2H_2O$$
  $\longrightarrow$   $ML_2.2H_2O$  (M = Ni or Co) (8)

The analytical data for the metal chelates along with their colour and molar conductivity values are listed in Table I. These data reveal that



Fig. 3. Correlation of logK<sub>1</sub> Values of Ligand SDD with Electronegativity of Metal Ions.



Fig. 4. Conductometric Titration of the Cu(II)-SDD System.



Fig. 5. Concentration Distribution of Various Species as a Function of pH in the Cu(II)-SDD System.

the ligand acts as a monobasic ligand, the complexes formed are formulated as MLC1.H<sub>2</sub>O,[ML<sub>2</sub>.2H<sub>2</sub>O]Cl and ML<sub>2</sub>.2H<sub>2</sub>O.

The molar conductance values of  $1 \times 10^{-3}$  M DMF solutions of the synthesized complexes are quite low and are in the range 5.7-12.2 ohm<sup>-1</sup>.cm<sup>2</sup>.mol<sup>-1</sup> which indicates the non-electrolytic nature of these complexes, except for the Cr(III)-complex ( $\Lambda = 69.7$  ohm<sup>-1</sup>.cm<sup>2</sup>.mol<sup>-1</sup>) which is considered as ionic due to the presence of chloride ion in the outer chelation sphere.

## **Infrared Spectra**

The fundamental IR vibrational bands of the ligand and their complexes are included in Table III. The IR spectrum of the ligand

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Table III. Fundame	otal IR Ba	ads (cm <sup>−^</sup> )	for the Li	gand (SUU	) and its h	detai com	piexes
Complex	V <sub>NH2</sub>	δ <sub>NH2</sub>	h <sub>N</sub> A	vso <sub>2</sub>	۰.M	۷м	<b>v</b> <sub>M-C1</sub>
SDD	3400 (br)	1600	3100 (w)	1350 (s)		1	1
CuLCI.H2O	3410	1687 (br)	l	1320	487 (s)	508 (s)	294 (w)
[CrL <sub>2</sub> .2H <sub>2</sub> 0]Cl	3405 (br)	1680	6 9 6	1325 (s)	455 (w)	505	-
NiL <sub>2</sub> .2H <sub>2</sub> O	3400	1670		1321	450 (w)	515 (w)	1
C₀L <sub>2</sub> .2H <sub>2</sub> O	3410 (br)	1685		1320	440 (s)	515 (s)	!
ZnLCI.H2O	3412 (br)	1665	1	1321 (w)	490	510 (w)	272 (w)
Hglc1.H2O	3402	1670 (m)	1	1320	445 (m)	510 (w)	275
CdLCI.H2O	3408 (w)	1675		1313 (w)	440	500	272
UO <sub>2</sub> LCI.H <sub>2</sub> O	3402	1685		1325	455	530	285 (s)
PdLCI.H2O	3410	1690	:	1330	460 (w)	515	280

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s: strong; m: medium; w: weak; br: broad.

# reveals a broad band near 3100 cm<sup>-1</sup> assignable to the intramolecularly hydrogen bonded sulfonamide NH group, as shown in Fig. 6.

A sharp, medium intensity stretching band at 3400 cm<sup>-1</sup> attributed to UNH<sub>2</sub> in the ligand is blue-shifted in the metal complexes. Also, the spectrum of the ligand shows a strong band at 1350 cm<sup>-1</sup> due to the SO<sub>2</sub> stretching vibration, This band was red-shifted in the spectra of the complexes indicating that the SO<sub>2</sub> group is participating in the complex formation. The presence of coordinated water molecules in the prepared complexes is indicated by the presence of a strong broad band in the region 3450-3300 cm<sup>-1</sup> attributable to the UOH stretching of coordinated water. The  $v_{sym}$  and  $v_{asym}(UO_2)$  bands are shifted to lower frequencies in the complex compared to uranyl nitrate for which the  $v_{asym}$  (O=U=O) mode appears<sup>14</sup> at 965 cm<sup>-1</sup>. Hence, we deduce that the ligand forms strong bonds with uranium, thereby effectively decreasing the U=O bond order and, consequently, lowering the  $v_{asym}$ (O=U=O) frequency. New bands around 490-440, 530-500 cm<sup>-1</sup> and 294-272 cm<sup>-1</sup> are seen in the spectra of complexes<sup>12-14</sup> which are assigned to  $\upsilon(M-O)$ ,  $\upsilon(M-N)$  and  $\upsilon(M-Cl)$ , respectively.

## Electronic Spectra

The electronic absorption spectra of the synthesized complexes were recorded in DMF. The electronic spectra of the Cu(II)-SDD complex in solution is characterized by a broad band within the 14780-13660 cm<sup>-1</sup> range due to the  ${}^{2}B_{1g} \leftarrow {}^{2}A_{1g}$  transition and a shoulder at approximately 20000 cm<sup>-1</sup> associated with the square-planar configuration for the Cu(II) complex<sup>18,19</sup>. The value of the magnetic moment (1.8 BM) could be considered as evidence for the square-planar geometry. The mass spectrum of the Cu(II)-SDD complex (Table 1)



Fig. 6. Intramolecular H Bond in SDD.

shows a weak parent ion peak at 393 amu (M.W. 394.0). The parent peak at 202 amu (100 %) corresponds to the ionic species left after elimination of phenylamine from the molecular ion.

The electronic spectra of the Cr(III) complex are similar, with major bands at 17050 and 22935 cm<sup>-1</sup>, while a third spin-allowed transition was not detected. From the observed electronic transition, the ligand field parameters Dq, B and  $\beta$  were calculated according to Lever<sup>20</sup> and are given in Table IV together with  $v_3$ (calcd). The Dq/B and  $v_2/v_1$  values are in agreement with values obtained for octahedral Cr(III) complexes<sup>21</sup>. The B value lies at approximately 590 cm<sup>-1</sup>. This indicates that there is considerable orbital overlap with the strongly covalent metal ligand bond.

The electonic absorption spectrum of the Ni(II) and the Co(II) complexes were recorded similarly and exhibited energy transitions consistent with octahedral geometry. The band assignments and the

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Table I

Complex	v <sub>1</sub> (cm <sup>-1</sup> ) assignment	v <sub>2</sub> (cm <sup>-1</sup> ) assignment	V <sub>3</sub> (cm <sup>-1</sup> ) assignment	v 1/v 1	Dq/B	10Dq cm <sup>-1</sup>	æ	β
[CrL <sub>2</sub> .2H <sub>2</sub> 0]Cl	$^{17050}_{4}\mathbf{A}_{2g}\rightarrow^{4}\mathbf{T}_{2g}$	23529 <sup>4</sup> A <sub>2g</sub> → <sup>4</sup> T <sub>1g</sub>	37175 <sup>4</sup> A <sub>2g</sub> → <sup>4</sup> T <sub>1g(p)</sub>	1.38	2.89	17050	590	0.64
CoL <sub>2</sub> .2H <sub>2</sub> O	9560 <sup>3</sup> A <sub>2 g</sub> → <sup>3</sup> T <sub>2 g</sub>	13440 <sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g(F)</sub>	24570 ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g(p)}$	1.42	1.25	9450	759	0.73
NiL <sub>2</sub> .2H <sub>2</sub> 0	6635 <sup>4</sup> T <sub>1g(F)</sub> → <sup>4</sup> T <sub>2g(F</sub>	14928 ). <sup>4</sup> T <sub>1g(F)</sub> → <sup>4</sup> T <sub>2g(F)</sub>	$17043$ ${}^{4}T_{1g} \rightarrow {}^{4}T_{1g(p)}$	2.25	1.11	8300	745	0.76

ligand field parameters are given in Table IV. These values are close to those shown by many octahedral Co(II) and Ni(II) complexes<sup>22,23</sup>. The octahedral configuration around Co(II) and Ni(II) is further confirmed by the magnetic moment values in Table I. The decrease in the B values of the Co(II) and Ni(II) complexes compared to that for the free ions (981 and 1030 cm<sup>-1</sup>), is evidence for considerable covalent character of these complexes.

The electronic spectra of the Zn(II), Hg(II) and Cd(II) complexes show main absorption bands at 43400, 38500 and 42100 cm<sup>-1</sup>, respectively<sup>24,25</sup>. These bands are assigned as chloride to metal charge transfer because most non-transition metal ion complexes are white and no low energy transition can take place within the atom and no transfer of electrons from the ligand to the metal can occur. Thus, from IR, electronic and the analytical data (Table I) it is clear that SDD reacts with Zn(II), Hg(II) and Cd(II) in 1:1 molar ratio with tetrahedral coordination around these metal ions.

The electronic spectrum of the  $UO_2(VI)$  complex exhibits a band at 22405 cm<sup>-1</sup> assigned to the  ${}^{1}Eg \rightarrow {}^{2}\Pi_{a}$  transition, corresponding to the O=U=O symmetric stretching frequency for the first excited state<sup>26</sup>. Also, the bands observed at 37800 and 29900 cm<sup>-1</sup> are assigned to the  $\Pi - \Pi^{*}$  and  $n - \Pi^{*}$  transitions, respectively<sup>27</sup>.

In the electronic spectrum of the Pd(II)-SDD complex in solution the first major band at 23800 cm<sup>-1</sup> is assigned to the  ${}^{1}A_{2g} \leftarrow {}^{1}A_{1g}$ transition  $b_{2g} \leftarrow b_{1g}$  and the second major band at 20200 cm<sup>-1</sup> to the  ${}^{1}B_{1g} \leftarrow {}^{1}A_{1g}$  transition  $a_{1g} \leftarrow b_{1g}^{28}$  associated with a square-planar configuration around Pd(II).

	Chen	nical Shifts	(δ ppm) <sup>a</sup>	
System	CH <sub>3</sub>	<sup>NH</sup> 2	ΝH	Aromatic ring
SDD	2.60 (6H, s)	6.11 (2H, s)	10.9 (1H, s)	6.1-6.8 (5H, m)
UO <sub>2</sub> LCI .H <sub>2</sub> O	2.50 (3H, s) 2.40 (3H, s)	6.10 (2H, s)		6.5-7.6 (5H, m)

Table V. <sup>1</sup>H NMR Chemical Shifts of SDD and the UO<sub>2</sub>(VI)-SDD Complex.

a; s = singlet, m = multiplet

## <sup>1</sup><u>H NMR Spectra</u>

The <sup>1</sup>H NMR spectrum of the ligand and UO<sub>2</sub>(VI)-SDD taken as a representative in DMSO is shown in Table V. The SDD spectrum a singlet signal at 10.9 ppm due to H of NH, its width exhibits indicating that it is probably involved in intramolecular hydrogen bonding (-N...H...O-). In the <sup>1</sup>H NMR spectrum of the UO<sub>2</sub>(VI)-SDD complex the latter signal has disappeared which is indicating clear evidence for the participation of the N atom in coordination. Also, the spectrum of SDD shows a singlet peak at 2.6 ppm due to the 6 protons of the 2 CH<sub>3</sub> groups. This signal is split into two signals, one at 2.50 ppm and the other at 2.40 ppm in the spectrum of the complex. In the latter the two methyl groups are magnitically non-equivalent as they suffer different electronic effects by the ortho and para nitrogen atoms. The presence of coordinated water molecules in the complexes is confirmed by the presence of a new signal at around 3.8 ppm, which has been attributed to H<sub>2</sub>O protons<sup>26</sup>. This is also supported by TGA which



UO<sub>2</sub> and Pd

Fig. 7. Structurs of the Metal Complexes.

indicates loss of water molecules in the temperature range 208-320°C. Further investigation to provide more convincing evidence for the structure of the complex is underway. The most probable structures for these complexes can be represented as shown in Fig. 7.

## **Conclusion**

The results of this study show that SDD in the complexes is uninegatively charged with a bidentate ON donor set forming 1:1 complexes with Cu(II), Zn(II), Hg(II), Cd(II), UO<sub>2</sub>(VI) and Pd(II) and 1:2 complexes with Cr(III), Ni(II) and Co(II).

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Received:	1 November 1995	Referee I:	P. R. Singh
Accepted:	23 October 1996	Referee II:	F. R. Johnston