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SYNTHESIS AND CHARACTERIZATION OF SOME THIOCYANATO COMPLEXES OF Ni(II), Cu(II), Pd(II), Pt(II), Au(III), Ti(III), AND V(IV) CONTAINING A TRIDENTATE SCHIFF BASE LIGAND

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ABSTRACT

A tridentate ligand HL having a ONN donor sequence has been synthesised by the condensation of ethylenediamine with salicylaldehyde. The ligand undergoes deprotonation during complexation and forms complexes of the compositions, [M(L)(SCN)], [M = Ni(II), Cu(II), Pd(II) and Pt(II), L = deprotonated Schiff base], K[Ti(L)(SCN)$_3$], [Au(L)-(SCN)]Cl and K[V(O)(L)(SCN)$_2$]. These complexes were characterized on the basis of elemental analyses, conductivity and magnetic measurements, NMR, infrared and electronic spectral studies. The magnetic and spectral data are consistent with square-planar stereochemistry for the Ni(II), Cu(II),

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Pd(II), Pt(II) and Au(III) complexes while the Ti(III) and V(IV) complexes are octahedral in nature.

INTRODUCTION

Many complexes of different Schiff bases have been reported by a number of authors.[1–10] These kinds of Schiff base ligands provide intriguing chemistry with both the lighter and heavier transition metals. We have extended our studies to a simple tridentate ONN ligand resulting from the condensation of ethylenediamine and salicylaldehyde.[9–10] In this paper we report the synthesis and characterization of thiocyanato complexes of Ni(II), Cu(II), Pd(II), Pt(II), Au(III), Ti(III) and V(IV) containing the tridentate ONN ligand. The structure of the Schiff base is shown in Fig. 1.

EXPERIMENTAL

Reagents

All chemicals used were of reagent grade and were used as supplied by E. Merck or BDH Ltd. Ethanol was purified by refluxing the 99% commercially available product with magnesium turnings and iodine.

Physical Measurements

Microanalyses for carbon, hydrogen and nitrogen were performed by the microanalytical services of the Department of Chemistry, University of St. Andrews, Scotland. The metals were determined by the standard literature procedures.[11] The IR spectra (KBr discs) were recorded on Shimadzu IR-470, Shimadzu FTIR-8400 and Perkin Elmer IR-470 spectrophotometers. ^{1}H NMR spectra in DMSO-d_6 were obtained with a Bruker DRX-400 (400.13 MHz) NMR spectrometer. Conductivities of

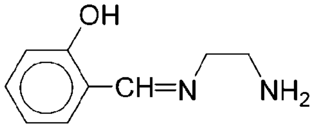

Figure 1. 4-(2-Hydroxy-phenyl)-3-aza-1-amino-3-butene.

10^{-3} M solutions in DMSO were measured at room temperature using a WPA CM 35 conductometer and a dip-type cell with platinized electrodes. Magnetic measurements have been carried out in a Johnson Mathey magnetic susceptibility balance at room temperature. Electronic spectra in DMSO were obtained on a LKB-Ultrospec K4053 spectrophotometer. Melting and decomposition points of the complexes have been determined on an electrothermal melting point apparatus.

Preparation of Schiff Base

Salicylaldehyde (0.61 g, 0.005 mol) in absolute ethanol (15 mL) was added to a solution of ethylenediamine (0.3 g, 0.005 mol) in the same solvent (20 mL). The mixture was heated on a water bath to reduce the volume of the solution to *ca.* 15 mL. The solution was then cooled to room temperature when yellow crystals were formed. These were separated and washed throughly with ethanol and dried in *vacuo* over P_4O_{10}. Yield, 0.7 g, (76%) m.p. 104–106 °C. Anal. Calc. for $C_9H_{12}N_2O$ (MW 164): C, 65.8; H, 7.3; N, 17.1. Found: C, 65.7; H, 7.3; N, 16.7%.

General Method for the Preparation of [M(L)(SCN)] [M = Cu(II), Ni(II), Pd(II), and Pt(II), HL = Schiff Base]

An appropriate solution of 0.005 mol of the metal salt ($CuCl_2 \cdot H_2O$, $NiCl_2 \cdot 6H_2O$, $PdCl_2$, $PtCl_2$) in absolute ethanol (25 mL) was added to an ethanolic solution (30 mL) of potassium thiocyanate (0.48 g, 0.005 mol). The solution was filtered and an ethanolic solution (80 mL) of HL (Schiff base) (0.82 g, 0.005 mol) was added to the filtrate. The resulting mixture was heated on a water bath for 5 min and cooled in an ice-bath. The complexes separated, were washed with hot ethanol and dried in *vacuo* over P_4O_{10}.

Preparation of $K[Ti(L)(SCN)_3]$

This complex was prepared by adding an ethanolic solution (15 mL) of $TiCl_3$ (0.77 g, 0.005 mol) to a solution of potassium thiocyanate (1.45 g, 0.015 mol) in the same solvent (45 mL). The solution was filtered and an ethanolic solution (60 mL) of HL (0.82 g, 0.005 mol) was added to the filtrate. The resulting mixture was boiled on a water-bath for 5 min and then cooled in an ice bath. The complex separated, was washed with hot ethanol and dried in *vacuo* over P_4O_{10}.

Preparation of [Au(L)(SCN)]Cl

A solution of $HAuCl_4$ (1.7 g, 0.005 mol) in ethanol (25 mL) was added to a solution of potassium thiocyanate (0.48 g, 0.005 mol) in the same solvent (30 mL). The solution was filtered and to the filtrate was added an ethanolic solution (50 mL) of HL (0.82 g, 0.005 mol). The complex separated and was washed successively with ethanol and ether and dried in *vacuo* over P_4O_{10}.

Preparation of K[V(O)(L)$(SCN)_2$]

A solution of $VO(SO_4)\cdot 5H_2O$ (1.26 g, 0.005 mol) in ethanol (25 mL) was added to a solution of potassium thiocyanate (0.97 g, 0.01 mol) in the same solvent (40 mL). The solution was filtered and to the filtrate was added an ethanolic solution (70 mL) of HL (0.82 g, 0.005 mol). The complex separated and was washed successively with ethanol and ether and dried as above.

RESULTS AND DISCUSSION

During the course of the reactions the Ni(II), Cu(II), Pd(II), Pt(II), Au(III), Ti(III) and V(IV) thiocyanates were first formed, and then coordinated to the Schiff base.

$$MCl_2 + 4KSCN \rightarrow K_2[M(SCN)_4] + 2K^+ + 2Cl^- \qquad (1)$$

$$K_2[M(SCN)_4] + HL \rightarrow [M(L)(SCN)] + H^+ + 2K^+ + 3SCN^- \qquad (2)$$

M = Ni(II) (**1**), Cu(II) (**2**), Pd(II) (**3**) and Pt(II) (**4**), HL = Schiff base.

Reaction Steps of Au(III) (**6**) Complex

$$HAuCl_4 + 4KSCN \rightarrow K_2[Au(SCN)_4]Cl + H^+ + 2K^+ + 3Cl^- \qquad (3)$$

$$K_2[Au(SCN)_4]Cl + HL \rightarrow [Au(SCN)]Cl + H^+ + 2K^+ + 3SCN^- \qquad (4)$$

Reaction Steps of Ti(III) (**5**) Complex

$$\mathrm{TiCl_3 + 6KSCN \rightarrow K_3[Ti(SCN)_6] + 3K^+ + 3Cl^-} \tag{5}$$

$$\mathrm{K_3[Ti(SCN)_6] + HL \rightarrow K[Ti(L)(SCN)_3] + 2K^+ + H^+ + 3SCN^-} \tag{6}$$

Reaction Steps of V(IV) (**7**) Complex

$$\mathrm{VO(SO_4) + 5KSCN \rightarrow K_3[VO(SCN)_5] + 2K^+ + SO_4{}^{2-}} \tag{7}$$

$$\mathrm{K_3[VO(SCN)_5] + HL \rightarrow K[VO(L)(SCN)_2] + H^+ + 3SCN^- + K^+} \tag{8}$$

Elemental Analyses and Conductivity

The analytical data and conductivity of the complexes are given in Tables I and II. All of the complexes are soluble in dimethyl sulfoxide but insoluble in water. The conductance values indicate that the complexes (**1**), (**2**), (**3**), (**4**) and (**6**) are all 1:1 electrolytes while the complexes (**5**) and (**7**) are 2:1 electrolytes.[12]

IR Studies

The infrared spectral data are shown in Table III. The Schiff base ligand is potentially tridentate, the available coordination sites being the amino nitrogen, methine nitrogen and the oxo anion. The free Schiff base shows characteristic bands at 3550 [ν(OH)], 3480, 3420 [ν(NH_2)] and 1615 cm^{-1}, [ν(C=N)]. In all of the complexes, a broad band appears at 3300–3600 cm^{-1}, in which ν(NH_2) bands of the complexes are probably hidden. The NH_2 complexation is inferred from the appearance of ν(M–N) modes at 430–472 cm^{-1} in the complexes.[2,13,14] We believe that the ligand deprotonates at the OH end providing oxo coordination, as is evident from the ν(M–O) bands at 480–542 cm^{-1} in the complexes. The ν(C=N) band observed at 1615 cm^{-1} in the free Schiff base ligand is shifted to 1577–1602 cm^{-1}, indicating coordination by the methine nitrogen.

Table I. Analytical Data[a]

No.	Empirical Formulas	Formula Weight	Yield (%)	Colour	Melting Point (°C)	% M	% C	% H	% N
(**1**)	[Ni(L)(SCN)]	279.69	65	Reddish	284–286	20.98	42.90	3.93	15.01
	$C_{10}H_{11}ONiN_3S$					(21.27)	(43.3)	(3.65)	(14.58)
(**2**)	[Cu(L)(SCN)]	284.5	60	Yellowish	114–116	22.31	42.17	3.86	14.76
	$C_{10}H_{11}OCuN_3S$					(22.59)	(42.55)	(4.23)	(15.14)
(**3**)	[Pd(L)(SCN)]	327.42	58	Brick red	190–192	32.50	36.65	3.35	12.82
	$C_{10}H_{11}OPdN_3S$					(32.86)	(36.94)	(3.64)	(13.24)
(**4**)	[Pt(L)(SCN)]	416.08	59	Yellow	112–114	46.88	28.84	2.64	10.09
	$C_{10}H_{11}OPtN_3S$					(47.23)	(29.32)	(3.03)	(10.41)
(**5**)	K[Ti(L)(SCN)$_3$]	423.75	62	Yellow	242–244	11.24	33.98	2.59	16.51
	$C_{12}H_{11}KOTiN_5S_3$				d	(11.62)	(34.35)	(3.04)	(16.85)
(**6**)	[Au(L)(SCN)]Cl	453.47	66	Ash	298–300	43.43	26.44	2.42	9.26
	$C_{10}H_{11}OClAuN_3S$				d	(43.72)	(26.81)	(2.63)	(9.63)
(**7**)	K[V(O)(L)(SCN)$_2$]	345.94	70	Grey	178–180	14.72	38.15	3.17	16.18
	$C_{11}H_{11}KO_2VN_4S_2$					(14.36)	(37.77)	(3.44)	(16.55)

[a] d = decomposition point. The found values are given in parenthesis.

Table II. Physical Properties

S. No. Complex	Complex	Molar Conductance ($Ohm^{-1}cm^2\ mol^{-1}$)	Magnetic Moment μ_{eff} (B.M.)
(**1**)	[Ni(L)(SCN)]	29	Dia.
(**2**)	[Cu(L)(SCN)]	32	1.95
(**3**)	[Pd(L)(SCN)]	34	Dia.
(**4**)	[Pt(L)(SCN)]	35	Dia.
(**5**)	$K[Ti(L)(SCN)_3]$	62	1.89
(**6**)	[Au(L)(SCN)]Cl	30	Dia.
(**7**)	$K[V(O)(L)(SCN)_2]$	65	1.69

The ambidentate thiocyanate ligand can coordinate either through the nitrogen or through the sulfur depending on the size of the metal ions. In general, the ν(CN) modes appear at lower frequencies in M–N=C=S complexes than those in M–S–C≡N complexes.[15,16] The complexes also display ν(CN) at 2077–2100 cm^{-1} characteristic of S-bonded thiocyanato moieties.[15,17,18] In Pearson's terminology, these are soft acids. The ν(CS) modes appear at lower frequencies in the M–S–C≡N complexes than those in the M–N=C=S complexes.[15,16]

Complexes (**1**)–(**7**) exhibit ν(CS) at 735–754 cm^{-1}, characteristic of a M–S–C≡N bonding sequence. This is further apparent from the ν(M–S) modes at 400–425 cm^{-1} in the far-IR spectra of the complexes.[2,13,19] The vanadium complex (**7**) displays a ν(V=O) mode[20,21] at 954 cm^{-1}.

Magnetic Moments and Electronic Spectra

The effective magnetic moments of the complexes are shown in Table II. The Cu(II), Ti(III) and V(IV) complexes are paramagnetic and show magnetic moments (1.69–1.95 B.M.) corresponding to one unpaired electron. The Ni(II), Pd(II), Pt(II) and Au(III) complexes are diamagnetic.

In the UV spectra three bands were observed at 15,350, 19,500 and 22,180 cm^{-1}, corresponding to the transitions $^2B_{1g}\rightarrow{}^2A_{1g}$, $^2B_{1g}\rightarrow{}^2E_g$ and charge transfer, respectively, for the Cu(II) complex. These bands are consistent with a square-planar structure.[22] The titanium(III) complex exhibits one characteristic d-d band at 19,550 cm^{-1} which corresponds to the transition $^2T_{2g}\rightarrow{}^2E_g$. This suggests an octahedral geometry with O_h symmetry of the Ti(III) complex.[23]

Table III. IR Spectral Data[a] of the Complexes (Band Maxima in cm^{-1})

Compound No.	ν(OH)	ν(C=N)	ν(NH_2)	ν(CS)	ν(M–O)	ν(M–N)	ν(CN)	ν(M–S)	Others
HL	3550 w	1615 m	3480 w 3420 w						
(**1**)		1600 s	3560–3400 br	754 s	542 m	472 s	2077 s	400 m	
(**2**)		1578 m	3600–3400 br	742 w	486 m	432 m	2100 w	410 w	
(**3**)		1600 s	3600–3300 br	745 vs	505 m	470 s	2090 s	410 w	
(**4**)		1577 s	3600–3400 br	742 s	486 m	432 m	2090 br	405 w	
(**5**)		1595 s	3600–3400 br	735 s	510 m	460 vs	2080 vs	425 w	
(**6**)		1598 s	3580–3400 br	738 m	540 m	430 w	2080 br	405 w	
(**7**)		1602 s	3600–3300 br	746 m	480 w	472 m	2096 vs	400 w	ν(V=O) 954 s

[a] Relative band intensities are denoted by s, m, w, vs, and br meaning strong, medium, weak, very strong, and broad, respectively.

Table IV. Electronic Spectral Data of the Complexes (Band Maxima in cm^{-1})

Compound No.	Band I	Band II	Band III	Band IV	Band V
(**1**)	21,114 (121)	–	–	–	–
(**2**)	15,350 (90)	19,500 (120)	22,180 (45)	–	–
(**3**)	22,155 (47)	28,170 (130)	31,115 (352)	35,000 (340)	40,150 (380)
(**4**)	36,075 (320)	39,510 (360)	41,112 (375)	–	–
(**5**)	19,550 (120)	–	–	–	–
(**6**)	33,885 (345)	40,220 (385)	–	–	–
(**7**)	17,825 (74)	22,124 (45)	33,112 (345)	39,200 (370)	–

Extinction coefficients in $dm^3 mol^{-1} cm^{-1}$ are given in parentheses.

The vanadium(IV) complex shows four bands at 17,825, 22,124, 33,112 and 39,200 cm^{-1}. The first two bands correspond to the transitions $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2A_1$, respectively, whereas the last two absorptions are caused by metal to ligand charge transfer. All of these bands are characteristic of an octahedral vanadium(IV) complex.[24,25] The Ni(II) complex displays a broad band at 21,114 cm^{-1} characteristic of a d-d transition ($^1A_{1g} \rightarrow {}^1B_{1g}$) for a singlet ground state of square-planar geometry.[26,27] The spectra of the Pd(II) complex in DMSO shows three spin-allowed d-d transitions and two charge transfer transitions. The bands were obtained at 22,155, 28,170, 31,115, 35,000 and 40,150 cm^{-1} corresponding to the transitions $^1A_{1g} \rightarrow {}^1A_{2g}$, $^1A_{1g} \rightarrow {}^1B_{1g}$, $^1A_{1g} \rightarrow {}^1E_g$, $^1A_{1g} \rightarrow {}^1A_{2u}$ and $^1A_{1g} \rightarrow {}^1E_u$, respectively, which indicates square-planar stereochemistry.[28] The Pt(II) complex gave three bands at 36,075, 39,510 and 41,112 cm^{-1} corresponding to the transitions $^1A_{1g} \rightarrow {}^1B_{1u}$, $^1A_{1g} \rightarrow {}^1E_u$ and $^1A_{1g} \rightarrow {}^1A_{2u}$, respectively. All of these bands are characteristic of a square-planar Pt(II) complex. The Au(III) complex gave two bands at 33,885 and 40,220 cm^{-1} corresponding to the transitions $^1A_{1g} \rightarrow {}^1E_u$ and $^1A_{1g} \rightarrow {}^1A_{2u}$, respectively, which indicates square-planar geometry.

^{1}H NMR Spectra

The ^{1}H NMR spectra of the Schiff base ligand and complex (**3**) were recorded in DMSO-d_6 solution at room temperature. All of these data are summarized in Table V.

^{1}H NMR spectra of the Schiff base ligand showed resonances corresponding to CH_2, NH_2, CH=N and OH protons, respectively. A singlet at

Table V. Proton NMR Spectral Data of the Schiff Base and Its Pd Complex (in ppm)

Compound	N=CH	OH Proton	NH_2	CH_2
Schiff base	8.54	13.33	6.83	3.87
Complex (**3**)	8.56		6.86	3.87

3.87 ppm corresponds to the four protons of the two CH_2 groups in diaminoethane. The CH=N proton resonance of the Schiff base ligand occurs as singlet at 8.54 ppm. For the NH_2 and OH group were singlets were observed at 6.83 and 13.33 ppm, respectively.

The ^1H NMR spectrum of (**3**) showed a downfield shift of the CH=N-azomethine hydrogen signal to 8.56 ppm compared to the free Schiff base ligand which supports the coordination of the azomethine nitrogen to the Pd(II) centre. Although the chemical shift difference between the ligand and the complex is not large, but all other supporting data *e.g.*, IR support the coordination of the ligand. The NH_2 protons resonance of complex (**3**) experienced a downfield shift to 6.86 ppm which also supports the coordination of the NH_2 group nitrogen to the Pd(II) centre. Coordination of the oxyanion (O^-) to the Pd(II) centre is suggested in the complex (**3**) on the basis of the disappearance of the OH proton signal. Thus, we assume that the disappearance of the OH proton resonance signal in complex (**3**) clearly indicates the coordination of the oxyanion (O^-) to the Pd(II) centre. This result is also supported by the IR data. The ^1H NMR spectra of the other complexes can also be explained in the same way.

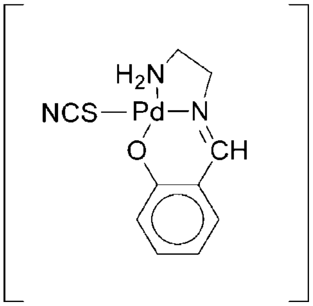

Figure 2. Proposed structure of the complex [Pd(L)(SCN)] (**3**).

The IR and ^{1}H NMR evidence allow us to construct a probable structure which is given in Fig. 2.

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