Some Novel Amino Acid-Schiff Bases and their Complexes Synthesis, Characterization, Solid State Conductivity Behaviors and Potentiometric Studies

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Three new Schiff bases derived from the condensation reaction of thiophene-2-carbaldehyde and DL-alanine, DL-valine and DL-phenylalanine have been synthesized and their Co(II), Ni(II) and Cu(II) complexes have been prepared. The Schiff bases and the complexes have been characterized by their analytical and spectral data. The protonation constants of the Schiff bases and stability constants of the complexes have been determined potentiometrically in aqueous medium at 25 °C and 0.1 M KCl ionic strength. Solid state conductivities of the synthesized substances were using the four-probe technique on a compressed pellet at room temperature.

Key words: Formation Constants, Schiff Bases, Metal Complexes, Potentiometry, Stability Constants

Introduction

Extensive investigations have been made on salicylidene amino acid Schiff bases and their metal complexes because of their possible use as potential **N**-pyridoxylidene amino acid systems [1-3]. Metal chelates of the Schiff bases derived from salicylaldehyde and amino acids have been shown to be important class of compounds in elucidating the mechanism of transamination reaction in biological systems [4, 5]. Thiophene containing Schiff bases are also widely studied [6-9], but no description of thiophene-amino acid Schiff bases has been published in the literature.

On the other hand, amino acid Schiff bases are sensitive to moisture and decompose when exposed to air, hence they are usually generated immediately prior to use for complexation. This is because only a small number of crystalline Schiff bases derived from amino acids and aldehydes can be isolated [10-13].

In the last decade, various electrically conductive substances have been studied extensively, among them a considerable number of polymers [14]. Conducting substances have attracted much attention from both fundamental and practical viewpoints. The study of aromatic substances that have a molecular structure containing π -bonds in chains is an active research area in the field of conducting substances [15].

Conductive substances have a number of potential technological applications in the areas of chemical transistors [16], including rechargeable batteries [17], electrochromic display devices [18] and biochemical analyses [19].

In a continuation of our previous work [20], in this work we report the synthesis and characterization of three new Schiff bases derived from the condensation of alanine, valine and phenylalanine with thiophene-2-carbaldehyde and their metal complexes with Co(II), Ni(II) and Cu(II) ions. In addition, the protonation constants of the Schiff bases and stability constants of their ML type complexes with Co(II), Ni(II) and Cu(II) determined by the potentiometric titrations are also reported here. The present study examines also the relationship between the solid state conductivity and the stability constants of Cu(II), Ni(II) and Co(II) complexes.

Results and Discussion

Schiff bases sodium salts 1-3 were synthesized from thiophene-2-carbaldehyde and DL-alanine, DLvaline and DL-phenylalanine, respectively. The ML type complexes of the Schiff bases were prepared using Co(II), Ni(II) and Cu(II) chloride. The molar conductance values of the Schiff bases and the complexes are

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Compound	Empirical formula	Color	Color Found (calcd.) %						λ
*	Decomp. temp. (°C)	$\mu_{(BM)}$	С	Н	Ν	S	Μ	Х	$(ohm^{-1} cm^2 mol^{-1})$
Na(tio-Ala).2H2O	NaC ₈ H ₁₂ NO ₄ S	yellow	40.34	4.99	6.02	13.51	-	-	51
	191 – 192	_	(39.83)	(4.98)	(5.81)	(13.28)			
Na(tio-Val)	NaC10H12NO2S	yellow	51.41	5.44	6.17	13.81	-	-	53
	194 – 195	_	(51.60)	(5.15)	(6.01)	(13.73)			
Na(tio-Phe).H ₂ O	NaC14H14NO3S	yellow	56.27	4.34	4.82	10.78	-	-	58
	196 – 197	_	(56.18)	(4.01)	(4.68)	(10.70)			
Na[Cu(tio-Ala)Cl2]	NaC8H8NO2SCl2Cu	light blue	28.41	2.45	4.27	9.32	18.82	20.93	58
	255	1.82	(28.27)	(2.35)	(4.12)	(9.42)	(18.70)	(20.91)	
Na[Cu(tio-Val)Cl2]	NaC10H12NO2SCl2Cu	light blue	32.58	3.51	3.41	8.90	17.42	19.37	58
	225	1.81	(32.65)	(3.26)	(3.27)	(8.71)	(17.28)	(19.32)	
Na[Cu(tio-Phe)Cl2].H2O	NaC14H14NO3SCl2Cu	light blue	38.69	3.17	3.12	7.30	14.51	16.60	57
	182	1.82	(38.75)	(3.23)	(3.23)	(7.38)	(14.65)	(16.38)	
Na[Ni(tio-Ala)Cl ₂ (H ₂ O) ₂]	NaC8H12NO4SCl2Ni	green	25.61	3.63	3.49	8.72	15.67	18.87	62
	208	3.30	(25.89)	(3.24)	(3.78)	(8.63)	(15.83)	(19.15)	
Na[Ni(tio-Val)Cl ₂ (H ₂ O) ₂]	NaC10H16NO4SCl2Ni	light green	29.83	4.21	3.58	8.32	14.31	17.59	67
	370	3.62	(30.10)	(4.01)	(3.51)	(8.03)	(14.72)	(17.81)	
Na[Ni(tio-Phe)Cl ₂ (H ₂ O) ₂]	NaC14H16NO4SCl2Ni	green	37.05	3.43	3.19	7.52	13.31	15.61	68
	384	3.21	(37.61)	(3.58)	(3.13)	(7.16)	(13.20)	(15.89)	
Na[Co(tio-Ala)Cl2]	NaC8H8NO2SCl2Co	deep blue	28.53	2.41	4.32	9.51	17.18	20.87	66
	256	4.48	(28.66)	(2.39)	(4.18)	(9.56)	(17.59)	(21.20)	
Na[Co(tio-Val)Cl2]	NaC10H12NO2SCl2Co	deep blue	33.31	3.38	3.83	8.79	16.11	16.30	64
	277	4.51	(33.09)	(3.31)	(3.86)	(8.82)	(16.24)	(19.58)	
Na[Co(tio-Phe)Cl2]	NaC14H12NO2SCl2Co	deep blue	40.64	2.90	3.56	7.94	14.72	17.61	61
	309	4.53	(40.88)	(2.92)	(3.41)	(7.79)	(14.33)	(17.28)	

Table 1. Analytical and physical data of compounds 1-3 and derived MCh complexes (M=Cu, Ni, Co).



Fig. 1. Structure of the Schiff bases 1-3.

found to be $50-68 \ \Omega^{-1} \ \text{cm}^2 \ \text{mol}^{-1}$ in $10^{-3} \ \text{M} \ \text{DMF}$ solutions, indicating the 1:1 electrolytic nature of the compounds [21]. The existence of sodium was determined qualitatively with a Flame Emission Spectrophotometer. The Schiff bases are pale yellow in colour and soluble in water, methanol and other polar solvents. The complexes are only slightly soluble in DMF and DMSO, but insoluble in other common organic solvents. All the compounds are stable in air. Analytical and physical data of the Schiff bases 1-3 and the dervied metal complexes are given in Table 1. UV/vis and characteristic IR data are shown in Table 2.

A medium intensity band in the higher frequency region is assigned to the v_{O-H} vibration of water in the Na(tio-Ala)·2H₂O and Na(tio-Phe)·H₂O. The strong absorptions at 1607–1598 cm⁻¹ and 1411–1401 cm⁻¹ are attributed to the asymmetric and symmetric v_{COO} bands. The azomethine stretching bands are observed in the range 1646–1641 cm⁻¹. The observation of a medium band at 634 cm⁻¹ may be attributed to the Schiff bases **1**–**3** in DMF show two bands at $\delta = 262 - 264$ and 284 nm asssignable to the π - π * transitions of the imine group and thiophene ring, respectively.

The ¹H NMR and ¹³C NMR data of the Schiff bases are collected in Table 3. In general, the multiplets observed at $\delta = 6.83 - 7.97$ ppm and the singlets at $\delta = 7.78 - 8.24$ ppm are assigned to thiophene ring protons and imine protons, respectively. The protons of methyl, isopropyl and benzyl groups of alanine, valine and phenylalanine amino acid residues of the Schiff

Table 2. Major IR absorbtion bands (cm⁻¹) and electronic spectral data (cm⁻¹) (ε_{max} . M⁻¹. cm⁻¹) of compounds 1–3 and derived MCL₂ complexes (M= Cu, Ni, Co).

Compound	v(OH)	v(CH=N)	<i>v</i> (COO ⁻¹)	$v(COO^{-1})$	v(C-S)	v(M-N)	v(M-O)	$\lambda_{\max/nm}(\varepsilon)$
			(asym)	(sym)				,
Na(tio-Ala).2H2O	3420	1643	1598	1411	634	-	-	$264 (1.5 \times 10^3), 284 (1.1 \times 10^3),$
Na(tio-Val)	-	1641	1607	1401	634	-	-	$262 (1.8 \times 10^3), 284 (2.3 \times 10^3),$
Na(tio-Phe).H ₂ O	3417	1646	1602	1410	633	-	-	264 (3.7×10^3) , 284 (2.9×10^3) ,
Na[Cu(tio-Ala)Cl ₂]	_	1633	1589	1392	633	518	464	$278 (9.3 \times 10^3)$, 383 (361), 698 (250)
Na[Cu(tio-Val)Cl ₂]	_	1625	1580	1393	632	520	461	$266 (5.8 \times 10^3), 382 (357), 694 (144)$
Na[Cu(tio-Phe)Cl ₂].H ₂ O	3450	1632	1582	1392	634	501	442	293 (5.3×10^3) , 390 (121), 696 (31)
Na[Ni(tio-Ala)Cl ₂ (H ₂ O) ₂]	3463	1632	1586	1393	632	531	463	267 (4.7×10^3) , 389 (10), 667 (2)
Na[Ni(tio-Val)Cl ₂ (H ₂ O) ₂]	3451	1625	1582	1394	634	532	462	$266(3.9 \times 10^3)$, 397 (159), 667 (45)
Na[Ni(tio-Phe)Cl ₂ (H ₂ O) ₂]	3430	1630	1586	1394	631	544	463	$275 (1.1 \times 10^3), 370(13), 693 (52)$
Na[Co(tio-Ala)Cl ₂]	_	1599	1536	1392	636	535	464	272 (2.65×10^3), 608 (1.89×10^2)
								$678 (2.42 \times 10^2)$
Na[Co(tio-Val)Cl ₂]	_	1616	1580	1410	634	532	464	$283 (2.39 \times 10^3), 608 (1.84 \times 10^2)$
								$674 (2.29 \times 10^2)$
Na[Co(tio-Phe)Cl ₂]	_	1601	1582	1394	632	544	450	279 (2.2×10^3), 607 (1.74×10^2)
								673 $(1.71 \times 10^2 \times 10^3)$

bases are also observed as expected. The occurence of E/Z isomerism at the imine band of the molecules [22] is also indicated by the NMR spectra; for example, two signals are observed for the NCH proton and the CH=N-CH carbon atoms, respectively.

The ¹H NMR spectrum of Na(tio-Phe)·H₂O shows additional splittings for the signals of methylene and methine protons became the methylene protons are diastereotopic. Due the different chemical environments, similar splitting is recorded for the protons of the methyl groups of the isopropyl moiety of **2**.

The ML₂ complexes of 1-3

The azomethine and carboxylate bands in the IR spectra of the complexes appear in the range 1599-1633, 1582-1589 and 1392-1410 cm⁻¹, somewhat lower than observed for the free ligands. These indicate that the azomethine nitrogen and the oxygen of the carboxylate group are coordinated to metal ion. All complexes exhibit a v(C-S-C) thiophene ring frequency that is almost unshifted relative to the free ligand (634 cm^{-1}) [23], suggesting that the sulphur atom of thiophene ring is not coordinated [24]. The IR specta of Ni(II) complexes exhibit characteristic bands of coordination water at ca. 3400, 882 and 768 cm⁻¹ assigned to v(OH), $\rho_r(OH)$ and $\rho_W(OH_2)$ vibrations, respectively [23]. These observations clearly suggest that the water molecules are coordinated to the nickel ion (Fig. 3). The appearance of new bands in the 544-531 and 463-462 cm⁻¹ regions due to v(M-O) and v(M-N), respectively [25].

The electronic spectra of the copper(II) complexes shows two d-d bands at *ca*. 690 nm and *ca*. 380 nm, indicating a square-planar stereochemistry. The absence of any bands below 1000 nm eliminates the possibility of tetrahedral geometry around the Copper(II) ion [26]. The molar magnetic moment values of the Copper(II) complexes vary in the range 1.80-1.81 BM. This indicates that the complexes are monomeric in nature and metal-metal interactions are absent.

Cobalt(II) complexes gave more intense bands in the d-d electronic spectra and high magnetic moment values between 4.48-4.53 B.M. which support a tetrahedral configuration [27]. All of the nickel(II) complexes show two d-d bands between 667-693 and 370-397 nm indicating an octahedral structure. The magnetic moment values between 3.11-3.62 BM observed for the Ni(II) complexes, provide further evidence of the octahedral nature around the Ni(II) ion [28]. TGA's of Na[Cu(tio-phe)Cl₂]·H₂O showed an endothermic peak in the temperature range 70-85 °C accompanied by weight loss of about 4.0%. The appearance of this peak may be accounted for by the presence of lattice water. Weight losses (about 8.5-9%) between 154-186 °C for all of the Ni(II) complexes are assigned to the loss of coordinated water [29]. The exothermic peaks lying at about 200-350 °C for all of the complexes were assigned to melting. In the 350-600 °C ranges, strong and broad exothermic peaks were observed for the complexes, characteristic of thermal degradation. The residues at the end of the decomposition for all of the complexes were found to be NaCl + NiO / CuO/ CoO.

			Compou	nd		
	Na(tio-Ala)∙	$2H_2O$	Na(tio-Va	l)	Na(tio-Phe)·H ₂ O	
Position	¹ H NMR	¹³ C NMR	¹ H NMR	¹³ C NMR	¹ H NMR	¹³ C NMR
1	3.84(d), 3.33(d)	69.82 ^a	3.13 (d), 2.90 (d)	68.98 ^a	3.72 (d), 3.98	64.34 ^a
	0.33 H, 0.66 H		0.40 H, 0.60 H		0.33 H, 0.66 H	
2	8.24 (s)	157.44 ^a	8.04 (s); 1 H	164.66 ^a	7.78 (s); 1 H	165.14 ^a
	1 H					
3	_	133.49	_	140.54	_	140.61
4	7.35-7.45 (d)	129.55	7.15 (d); $\Sigma = 1$ H	136.74	7.54 (d) $\Sigma = 1 \text{ H}$	134.75
	$\Sigma = 1 \text{ H}$					
5	7.02-7.15 (dd)	128.43	6.83 (dd); $\Sigma = 1$ H	135.60	7.06 (dd); $\Sigma = 1$ H	133.96
	$\Sigma = 1 \text{ H}$					
6	7.83-7.84 (dd)	130.62	7.63 (d); $\Sigma = 1$ H	137.31	7.97 (d); $\Sigma = 1$ H	137.26
	$\Sigma = 1 \text{ H}$					
7	_	181.24	_	187.91	_	186.87
a / b / d	1.17 (d), 1.29 (d)	19.77	1.88 (m),1.70 (m)	38.63	3.36 (m), 2.94 (m)	46.23
	0.33 H, 0.66 H		0.40 H, 0.60 H		0.66 H, 1.34 H	
c	_		0.62 (m); $\Sigma = 3$ H	25.32	_	
c'	_		0.51 (m); $\Sigma = 3$ H	25.86	_	
e-j	_				7.03-7.98 (m)	138.51, 129.00, 129.34,
-						128.71, 128.00, 126.3

Table 3. ¹H and ¹³C NMR chemical shifts (ppm) of the Schiff bases 1-3 (in CD₃OD).

^a Two signals.



Fig. 2. Structure of the MCl_2 complexes derived from Schiff bases 1-3.

Based on the above spectroscopic, analytical and the other data it can be concluded that, the Schiff bases are bidentate involving the azomethine nitrogen and carboxyl oxygen atoms. The other coordination sites are occupied by Cl^- for Cu(II) and Co(II) complexes, Cl^- and H_2O for Ni(II) complexes. Structures proposed for the complexes are shown in Figure 2.

Potentiometric studies

Potentiometric titration curves of solution mixtures i), ii) and iii) described in the Experimental Section, for Na(tio-Val) Schiff base and their complexes are given in Fig. 3; the values of all the constants are given in Table 4.

The shape of the titration curve of the [Na(tio-Val)] Schiff bases indicate that one proton neutralizes before the pH=4 and the other neutralizes in the pH region about 8-10. The first neutralization (logK₂^H)

Table 4. Protonation constants, stability constants and conductivity measurements of the Schiff bases and the complexes at 25 ± 0.1 °C.

Compound	log K ₁ ^H		(9 -1)
	$\log K_2^{11}$	log K _{ML}	σ (S cm ⁻¹)
	log K ₃ ^H		
Na(tio-Ala)·2H ₂ O	9.28 ± 0.01		$\sim 10^{-8}$
	3.05 ± 0.03		nonconductivty
Na(tio-Val)	9.34 ± 0.02		$\sim 10^{-8}$
	3.28 ± 0.02		nonconductivty
Na(tio-Phe)·H2O	9.10 ± 0.02		$\sim 10^{-8}$
	2.74 ± 0.03		nonconductivty
Na[Cu(tio-Ala)Cl]		9.89 ± 0.02	3.18×10^{-6}
Na[Cu(tio-Val)Cl]		10.17 ± 0.02	$4.11 imes 10^{-6}$
Na[Cu(tio-Phe)Cl] H ₂ O		8.72 ± 0.03	$5.21 imes10^{-6}$
Na[Ni(tio-Ala)Cl ₂ (H ₂ O)]		7.21 ± 0.03	$6.40 imes10^{-6}$
Na[Ni(tio-Val)Cl2(H2O)]		6.81 ± 0.02	$5.22 imes 10^{-6}$
Na[Ni(tio-Phe)Cl ₂ (H ₂ O)]		4.77 ± 0.01	$6.35 imes10^{-6}$
Na[Co(tio-Ala)Cl]		5.24 ± 0.02	$2.03 imes 10^{-6}$
Na[Co(tio-Val)Cl]		5.49 ± 0.02	$3.31 imes 10^{-6}$
Na[Co(tio-Phe)Cl]		4.88 ± 0.01	$3.79 imes10^{-6}$

refers to protonation of the carboxylate anion and the second neutralization $(\log K_1^H)$ to protonation of the imine nitrogen atom. First and second protonation constants of the Schiff bases increase in the order as $[Na(tio-Phe)] \cdot H_2O < [Na(tio-Ala)] \cdot 2H_2O < [Na(tio-Val)]$. This can be explained as follows: because of the electron donating effect of the R group, electron density of the carboxylate anions and imine nitrogens of the Schiff bases increases. The electron donating effect of the isopropyl group is higher than that of methyl and



Fig. 3. Potentiometric titration curves of Na(tio-Val) and Cu^{II} , Ni^{II}, Co^{II} complexes.

benzyl groups, with the latter having the lowermost effect.

Stability constants of the complexes of the three ligands with the same metal ion also showed the same order as protonation constants. This is an expected result, since electron donating groups increase the basicity of the donor atoms, hence the chelation ability of the ligands increase. The order of the stability constants for the same ligand with different metal ions, are found to be Co(II) < Ni(II) < Cu(II), in conformity with the Irving-Williams order for bivalent ions [30].

Solid state conductivity measurements

Solid state electrical conductivity results in the Table 4 show that the complexes are semi-conductive although the Schiff bases 1-3 do not conduct. The conductivities of the nickel(II) complexes are higher than the others. This may be attributed to the coordinated water in these complexes. H₂O may play a role as some sort of carrier hopping site [31]. All three metal complexes of the Na(tio-Phe)·2H₂O Schiff base (3) have the highest conductivity value in their set contrary to the order of their stability constants. This may be ascribed to the conjugation length in complexes arising from delocalization of π -electrons in the chelate ring. The smaller stability constants of these complexes may be due to the lower electron donating effect of the benzyl group. The conjugation length in complexes may lead to higher conductivity [32]. The conductivity values of the complexes are almost comparable with those of the complexes in our previous work [20]. So the exchange of the heteroatom from O to S in the Schiff bases does not play an important role in the conduction mechanism. Similarly, the number of unpaired electrons of the metal ions seems also not to be of importance for the conductivity behaviour.

Moreover, these metals improve interchain charge transfer, *e.g.*, high molecular weight complexes show high conductivities due to intermolecular charge transfer [33]. On the other hand, copper (II) complexes are more conductive than cobalt(II) complexes. These results may be due to the higher stability constants of the copper(II) complexes in comparison to cobalt(II) complexes.

Experimental Section

Physical measurements

¹H and ¹³C NMR spectra of the ligands were recorded with a Bruker Spectrospin Avance DPX-400 using TMS as internal standard and CD₃OD as solvent. IR spectra in the 4000-400 cm⁻¹ range were recorded using KBr discs on a Mattson 1000 FTIR spectrophotometer: Carbon, hydrogen and nitrogen values were obtained using a LECO-9320 analyser. Conductivity measurements were carried out at 20 °C in 10^{-3} M AcOH-DMF (1:9 v/v) using a Siemens WPA CM 35 apparatus. The DTA curves were obtained with a Netzsch Gerätebau apparatus between 20-600 °C with 10 °C min⁻¹. The TGA curves were obtained on General V4.1C Du Pont 2000 between 30-600 °C at a heating rate of 10 °C min⁻¹ in nitrogen atmosphere. The room temperature magnetic moments were measured with a MK-1 model Gouy Balance (Christison Scientific Equipment Ltd). Chlorine was determined titrimetrically with the Mohr method. Metals were determined with a Philips PU 9285 model AAS spectrophotometer.

Preparation of the sodium salts of the Schiff bases 1-3

Thiophene-2-carbaldehyde (0.95 ml, 10 mmol, d = 1.2 g/ml) in methanol (20 ml) was added dropwise to the solution of the DL-amino acid (10 mmol) dissolved in 2 M NaOH (5 ml). The mixture was heated under reflux for two hours. After cooling, the mixture was filtered and evaporated under reduced pressure until an oily like syrup had formed. This was dissolved in dioxane-methanol (9:1, v/v) and stirred magnetically for two days at 15 °C. The oily crude product was dissolved in a minimum amount of dioxane and precipitated by the addition of acetone. The final product was filtered, washed with acetone and dried *in vacuo* at room temperature. Yields are between 73 – 78%.

Preparation of the complexes

5 mmol of the DL-amino acid dissolved in 30 ml of water was added to 5 mmol of thiophene-2-carbaldehyde dissolved in methanol (60 ml). The solution was stirred magnetically and heated at 70 $^{\circ}$ C for three hours. The metal(II) chloride (5 mmol) dissolved in 20 ml of methanol was added to the solution of the Schiff base. 5 mmol of NaOH dissolved in

water (10 ml) was added dropwise to the reaction mixture and it was then stirred and heated again for three hours at 50 °C. The mixture was kept for two days at room temperature. The solid product was filtered, washed with water and acetone-water (1:1) solutions and dried *in vacuo* at 50 °C. Yields are between 83-72%.

Potentiometric reagents and solutions

Triply distilled water was used as solvent. All metal ion solutions were prepared from their analytical grade chlorides and standardized by the atomic absorption spectroscopic method. A standard 0.051 M KOH solution (Merck) was used for titrations. KCl (Merck, extra pure) and concentrated HCl (Merck, extra pure) were used for preparation of 1.0 M KCl and 0.056 M HCl solutions. HCl solution was standardized against standard KOH solutions. Alkali solutions were stored under nitrogen atmosphere.

Potentiometric measurements

Measurements were carried out using a Janway pH-meter equipped with a Janway combined glass electrode. The system was calibrated to read hydrogen ion concentration by titration of a hydrochloric acid solution at 25 ± 0.1 °C and 0.1 M KCl ionic strength with KOH solution according to Gran's method [34]. Small amounts ($\Delta v = 0.05$ ml) of titrant KOH solution were added with a microburette. Sample solutions were titrated in a double walled glass cell maintaned at $25\pm$ 0.1 °C in nitrogen atmosphere. Titrations were performed over the pH ranges 2.0-11.0 for the ligand sand 2.0–9.0 for the complexes using 25 ± 0.01 cm³ samples. There was no precipitation within the pH range for the titrations performed. The concentration of the ligands was $4.0.10^{-\bar{3}}\ M$ and metal-to-ligand molar ratio was 1:4. The following solutions were titrated potentiometrically against 0.051 M KOH: i) HCl+KCl, ii) HCl+KCl+ligand and iii) HCl+KCl+ligand+metal ion. PKAS and BEST computer programs were used for determination of the protonation constans of the ligands and stability constants of the ML type

- M. M. T. Khan, R. I. Kureshy, N. H. Khan, Tetrahedron: Asymmetry 2, 1015 (1991).
- [2] H. Qing-Yu, M. Zhen-Hua, Z. Ya-Mei, J. Coord. Chem. 21, 199 (1990).
- [3] P.K. Sharma, S.N. Dubey, Ind. Chem. Soc. 72, 577 (1995).
- [4] M. Nath, R. Yadov, Bull. Chem. Soc. Jpn. 70, 1331 (1987).
- [5] Z.H. Chrohan, S. Kauger, Met. Based. Drugs 7, 17 (2000).
- [6] J. García-Tojal, J. L. Pizarro, A. García-Orad, A. R. Pérez-Sanz, M. Ugalde, A. A. Díaz, J. L. Serra, M. I. Arriortua, T. Rojo, J. Inorg. Biochem 86, 627 (2001).

Solid state conductivity measurements

Solid state electrical conductivities (σ) were measured with a Nippon NP-900 multimeter using the four-probe technique. Solid state electrical conductivity may be defined as the ratio J/E of net charge motion, J (current density), brought about by an electric field E.

$$\sigma = J/E$$

The four-probe technique used for measuring the solid-state conductivity of pressed pellets was developed by van der Pauw [20]. Here, four points of contact, almost equally spaced on the periphery of the sample, were made with a conductive paste such as electrodag. The current (i) was passed through two adjacent contacts while the voltage drop (V) was measured across the other two as shown in Figure 4.

$$V$$
 Fig. 4. Van der measurement of

The van der Pauw technique takes into account the sam-

Pauw technique for the

ple thickness (d) and thus it must be measured along with the current-voltage characteristics of the samples. The formula employed for the measurement of conductivity is

$$\sigma = \ln 2/\pi d \cdot I/V.$$

The pellets of the Schiff bases and the complexes were prepared at a loading of *ca*. 7 tons and thickness of *ca*. 0.05 cm.

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- [7] A. S. Demir, Ö. Reis, M. Emrullahoğlu, Tetrahedron 58, 8055 (2002).
- [8] Y. Ishikawa, T. Miyamoto, A. Yoshida, Y. Kawada, J. Nakazaki, A. Izuoka, T. Sugawara, Tetrahedron Lett. 40, 8819 (1999).
- [9] J. Chen, R.J. Angelici, Inorg. Chim. Acta 334, 204 (2002).
- [10] E. Leporati, J. Coord. Chem. 33, 179 (1994).
- [11] H. Qing-Yu, M. Zhen-Hua, Z. Ya-Mei, J. Coord. Chem. 21, 199 (1990).
- [12] P. Gürkan, N. Sarı, Synt. React. Inorg. Met. Org. Chem. 29, 753 (1999).

- [13] I. Sakıyan, T. Gündüz, N. Gündüz, Synth. React. Inorg. Met. Org. Chem. **31**, 1175 (2001).
- [14] Ě. T. G. Cavalheiro, M. Ionashiro, G. Marino, S. T. Breviglieri, G.O. Chierice, Trans. Met. Chem. 25, 69 (2000).
- [15] B. Sarı, M. Talu, Turk. J. Chem. 22, 301 (1998).
- [16] I.S. Hutchinson, S.A. Matlin, A. Mete, Tetrahedron 58, 3137 (2002).
- [17] R. V. Hoffman, M. M. Reddy, C. M. Klumas, J. Org. Chem. 63, 9128 (1998).
- [18] S. Naitoh, K. Sanui, N. Ogata, J. Electroanal. Chem. Commun. 1349 (1986).
- [19] R. Lima, L. R. Teixeira, H. Beraldo, A. B. Almeida, C. L. Donnici, J. D. Fabris, Trans. Met. Chem. 25, 338 (2002).
- [20] N. Sarı, P. Gürkan, Trans. Met. Chem. 28, 468 (2003).
- [21] W.S. Geary, Coord. Chem. Rev. 7, 81 (1971).
- [22] R. M. Silverstein, G. C. Bassler, T. C. Morrill, Spectrophotometric Identification of Organic Compounds, 4th ed., Wiley, New York (1981).
- [23] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th ed., Wiley, New York (1986).

- [24] A. Çukurovali, I. Yilmaz, M. Ahmedzade, H. Özmen, Synth. React. Inorg. Met. Org. Chem. 31, 255 (2001).
- [25] A. N. Speco, M. Karayanis, L. L. Pylywski, Inorg. Chim. Acta 9, 87 (1977).
- [26] A. P.B. Lever, Inorganic Electronic Spectroscopy, 2nd ed., Elsevier, Amsterdam (1982).
- [27] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 3th ed., Wiley, New York (1972).
- [28] A. M. Abdel-Mavgoud, Synth. React. Inorg. Met. Org. Chem. 21, 687 (1991).
- [29] R. K. Ray, J. Thermal Analysis, 36, 455 (1990).
- [30] H. Irving, R. J. Williams, J. Chem. Soc. 3192 (1952).
- [31] T. Ohsawa, K. Kaneto, K. Yoshino, Jpn. J. Appl. Phys. 9, L663 (1984).
- [32] K. Kaneto, K. Yoshino, Y. Inuishi, Jpn. J. Appl. Phys. 22, L412 (1983).
- [33] S. Venkatachalam, V. N. Krishnamurthy, Ind. J. Chem. 33A, 506 (1994).
- [34] G. Gran, Analyst 77, 661 (1952).
- [35] A. E. Martell, R. Motekaitis, Determination and Use of the Stability Constants, VCH Publishers, New York (1988).