

Electrochemical Behavior of N₂SO Schiff-Base Co(II) Complexes in Non-Aqueous Media at the Surface of Solid Electrodes

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The electrochemical behavior of three newly synthesized Schiff-base Co(II)-complex with N₂SO donor group was investigated. In different non-aqueous media such as acetonitrile (AN) and %50w/w dichloromethane-dimethylsulfoxide (CH₂Cl₂-DMSO) mixture as aprotic solvents at the surface of solid electrodes (Pt, Au and GC) using tetrabutylammonium perchlorate as supporting electrolytes electrochemical behavior studied by cyclic voltametry. It has been found that, these compounds exhibit one or two quasireversible oxidation peaks and the charge transfer coefficients (α) and the diffusion coefficients (D) for these compounds in various solvents were obtained. The effect of scan rate and dielectric constant of solvents on the redox behavior of compounds were evaluated.

Keywords: Schiff Base; Electrochemical Behavior ; Solid Electrodes; Cyclic Voltametry

1. INTRODUCTION

Schiff bases have often been used as chelating ligands in the field of coordination chemistry and their metal complexes are of great interest for many years. It is well known that N and S atoms play a key role in the coordination of metals at the active sites of numerous metallobiomolecules [1]. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer and herbicidal applications [2]. They serve as models for biologically important species and find applications in biomimetic catalytic reactions. Chelating ligands containing N, S and O donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions. It is known that the existence of metal ions

bonded to biologically active compounds may enhance their activities [3-4]. The variety of possible Schiff base metal complexes with wide choice of ligands, and coordination environments, has prompted us to undertake research in this area [5]. In the literature review, there is papers in the synthesiss, characterization and study of the electrochemical behavior of new Schiff-base [6-10] and other compounds at the surface of different solid electodes and medias [11-15]. As a part of our continuing work on dissymmetric tetradentate Schiff base complexes containing N, S and O donor atoms [16-17] and our research group in the recent years [18-20], we now report the synthesis and characterization of three Co (II) complex of the tetradentate unsymmetric Schiff base ligand such as Co(pytaOMe), Co(pytaBr) , Co(pytaNO₂) and a brief study of its electrochemical behavior with the different solid electrodes in aprotic solvents.

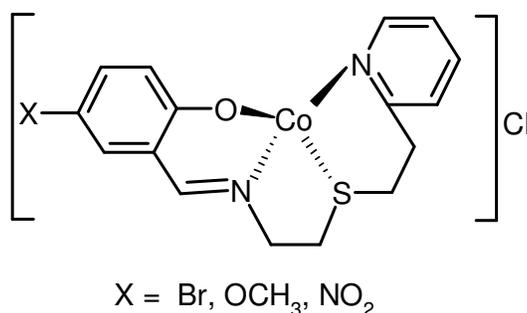


Figure 1. Chemical structure of tested compounds

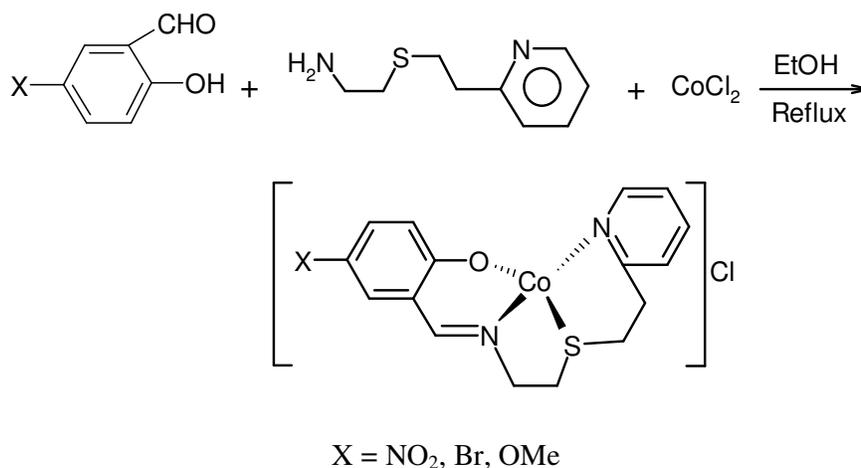
2. EXPERIMENTAL PART

2.1. Reagents and techniques

All the chemicals and solvents used for the syntheses were of reagent grade and were obtained commercially from Merck Company with the exception of the cadmium nitrate, which was obtained from Aldrich. The solvents were purified by standard methods. The ligand (PytBrsalH) was synthesized and characterized according to a published method [16] from 1-(2-pyridyl)-3-thia-5-aminopentane (pyta) [17-18] and 2-vinyl pyridine distilled in vacuum before use. The infrared spectra of the ligand and complexes were recorded on a Shimadzu Prestige 21 FT-IR spectrometer as KBr disks. Elemental CHN analyses were performed using a Heraeus CHN-O-RAPID elemental analyzer. ¹H NMR and spectral measurements were carried out on a Bruker Spectrospin Avance 400 MHz ultrashield spectrometer with TMS as an internal reference. The conductivity measurements were carried out in acetonitrile at room temperature using a Hanna HI 8828Nconductometer. The electronic spectra of the compounds were recorded in acetonitrile on a Perkin-Elmer Lambda 25 (UV-Vis) spectrophotometer.

2.2. The synthesis of Co(II)- complexes

A solution of the ligand was prepared by either dissolving the required amount of the ligand (1 mmol) in absolute ethanol (10 mL) or by preparing the ligand *in situ* from its precursors as follows: a solution of pyta (1 mmol) in absolute ethanol (5 mL) was added to solution of 2-hydroxy-5-bromobenzaldehyde (1 mmol) in absolute ethanol (5 mL) and the mixture was refluxed for 40 min and then 1 M methanolic NaOH (1 mL) was added and reflux and stirring were continued for a further 3 min. Then $\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$ (1 mmol) in absolute ethanol (5 mL) was added to the ligand solution with stirring and the reaction mixture was further stirred under reflux for 30 min.



Scheme 1: Schematic representation of metal complex formation.

The obtained colored solution was left standing at room temperature to crystallize. The product was removed by filtration, washed with cooled absolute ethanol, recrystallized from acetonitril or methanol and dried under vacuum. The analytical and physical data of the complexes are:

$[\text{Co}(\text{PytBrsal})]\text{Cl}$ - Empirical formula: $\text{C}_{16}\text{H}_{16}\text{BrClN}_2\text{OSCo}$; formula weight: $458.729 \text{ g mol}^{-1}$; yield: 66%; appearance: yellowish microcrystals; m.p. = $165\text{-}166 \text{ }^\circ\text{C}$ (decomposed); Elem. analysis: calc. C, 3.10 %; H, 36.40 %; N, 5.20 %; found: C, 41.45 %; H, 3.49 %; N, 6.13%; FTIR: 3049 cm^{-1} $\nu_{(\text{C-H})}$ aromatic, $2860\text{-}2916 \text{ cm}^{-1}$ $\nu_{(\text{C-H})}$ aliphatic, 1622 cm^{-1} $\nu_{(\text{C=N})}$ iminic, 1285 cm^{-1} $\nu_{(\text{C-O})}$ phenolic. mol. conductivity: $143 \mu\text{S}$; electronic spectrum: 670 nm ($135 \text{ mol}^{-1}\text{Lcm}^{-1}$), 590 nm ($202 \text{ mol}^{-1}\text{Lcm}^{-1}$), 518 nm ($357 \text{ mol}^{-1}\text{Lcm}^{-1}$), 329 ($10400 \text{ mol}^{-1}\text{Lcm}^{-1}$), 229 ($34225 \text{ mol}^{-1}\text{Lcm}^{-1}$).

$[\text{Co}(\text{PytOMesal})]\text{Cl}$ - Empirical formula: $\text{C}_{17}\text{H}_{19}\text{ClN}_2\text{O}_2\text{SCo}$; formula weight: $409.863 \text{ g mol}^{-1}$; yield: 66%; appearance: yellowish microcrystals; m.p. = $202 \text{ }^\circ\text{C}$ (decomposed); Elem. analysis: calc. C, 41.32 %; H, 3.47 %; N, 6.02 %; found: C, 41.45 %; H, 3.49 %; N, 6.13%; FTIR: 3049 cm^{-1} $\nu_{(\text{C-H})}$ aromatic, $2860\text{-}2916 \text{ cm}^{-1}$ $\nu_{(\text{C-H})}$ aliphatic, 1622 cm^{-1} $\nu_{(\text{C=N})}$ iminic, 1285 cm^{-1} $\nu_{(\text{C-O})}$ phenolic. mol. conductivity: $143 \mu\text{S}$; electronic spectrum: 665 nm ($174 \text{ mol}^{-1}\text{Lcm}^{-1}$), 590 nm ($170 \text{ mol}^{-1}\text{Lcm}^{-1}$), 527

nm ($223 \text{ mol}^{-1}\text{Lcm}^{-1}$), 410 ($4737 \text{ mol}^{-1}\text{Lcm}^{-1}$), 329 ($9725 \text{ mol}^{-1}\text{Lcm}^{-1}$), 251 ($25337 \text{ mol}^{-1}\text{Lcm}^{-1}$), 226 ($28700 \text{ mol}^{-1}\text{Lcm}^{-1}$)

[Co(PytNO₂sal)Cl] - Empirical formula: C₁₆H₁₆ClN₃O₃SCo; formula weight: 424.834 g mol⁻¹; yield: 56%; appearance: yellowish microcrystals; m.p. = 251 °C (decomposed); Elem. analysis: calc. C, 41.32 %; H, 3.47 %; N, 6.02 %; found: C, 41.45 %; H, 3.49 %; N, 6.13%; FTIR: 3049 cm⁻¹ $\nu_{\text{(C-H)}}$ aromatic, 2860-2916 cm⁻¹ $\nu_{\text{(C-H)}}$ aliphatic, 1622 cm⁻¹ $\nu_{\text{(C=N)}}$ iminic, 1285 cm⁻¹ $\nu_{\text{(C-O)}}$ phenolic. mol. conductivity: 142 μS ; electronic spectrum: 675 nm ($102 \text{ mol}^{-1}\text{Lcm}^{-1}$), 620 nm ($175 \text{ mol}^{-1}\text{Lcm}^{-1}$), 510 nm ($386 \text{ mol}^{-1}\text{Lcm}^{-1}$), 360 ($21375 \text{ mol}^{-1}\text{Lcm}^{-1}$), 253 ($23175 \text{ mol}^{-1}\text{Lcm}^{-1}$), 240 ($20583 \text{ mol}^{-1}\text{Lcm}^{-1}$)

2.3. Electrochemistry

Cyclic voltametric measurements and microelectrolysis at controlled potential experiments were performed using a potentiostat – galvanostat Auto-Lab instrument equipped with a three electrode system in an undivided cell. Pt-disk or Au and glassy carbon polished electrodes were used as working electrodes. The reference was an aqueous saturated calomel electrode (SCE), separated from the bulk of the solution by a bridge filled with solvent and supporting electrolyte. Solutions in the bridge were changed periodically to avoid aqueous contamination from entering the cell via the SCE. The auxiliary electrode was a Pt-wire coil. The electrolytic medium consisted of 0.1 M Bu₄NClO₄ in DMF and electroactivity range for this system was 3.4 V (from 1.5 to -1.5 V vs SCE). All solutions were deoxygenated by passing a stream of pre-purified N₂ into the solution for at least 10 Min prior to recording the voltamogram. Voltammetric measurements were performed at room temperature in Acetonitril (AN) and (CH₂Cl₂ + (CH₃)₂SO) solution with 0.1 M tetrabutylammunium perchlorate as the supporting electrolyte.

3. RESULTS AND DISCUSSION

3.1. The surface effect of electrode

For investigation surface effect on the electrochemical behavior of these compounds their cyclic voltamograms were recorded at the surface of different solid electrodes such as pelatin (Pt), gold (Au) and glassy carbon (GC). The typical results for 0.001 M solution of [Co (PytaNO₂)] are shown in Fig.1. That is obvious from Fig.1, the Pt electrode in this media is inert thus there is no detectable peak at the surface of this electrode. At the surface of other solid electrodes such as GC and Au are good media and active area for redox behavior of these new compounds. The gold electrode has been widely used in electrochemical studies and electroanalysis for various substrate for a long time because of its stability, wide potential window and fast electron transfer rate [21-22]. Thus, in this work we used the glassy carbon as working electrode for further experiments.

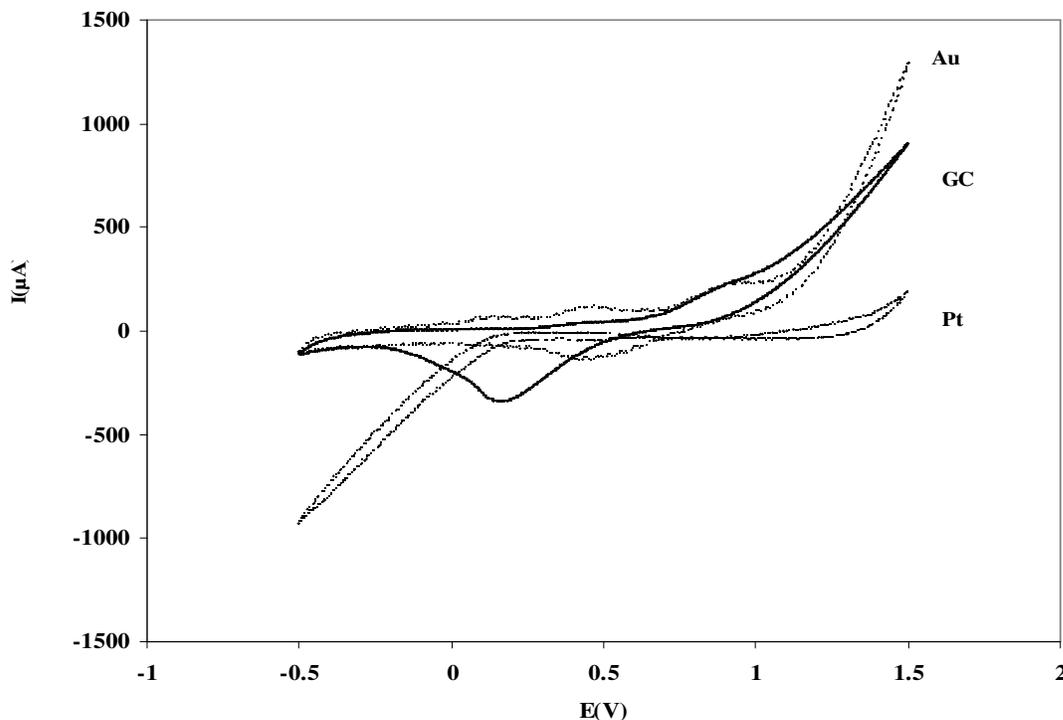


Figure. 2. Cyclic voltammograms of [Co (PytaNO₂)] in 0.1 M TBAP- (CH₂Cl₂ + (CH₃)₂SO) between -1.0 and 2.00 V in the scan rates 10 mV/S at the surface of different solid electrodes

3.2. The effect of structure

The electrochemical properties of compounds were highly sensitive to the bulk of solution and the electronic density at the ligand. The three ligands, PytaOMe, PytaNO₂ and PytaBr, are irreversibly oxidised in both solvents, the respective anodic peak potentials (scan rate 0.01 V/s) are approximately 1.22, 1.26 and 1.20 V in AN, and 1.17, 1.15 and 1.20 V in (CH₂Cl₂ + (CH₃)₂SO). With increasing scan rates all ligands show a positive peak potential shift, as well as an increase in current intensity. Although no comparison between the potential peaks values of the three ligands can be made due to the irreversible nature of charge transfer.

Cyclic voltammetric data for mM concentrations of three compounds in the surface of glassy carbon electrode are summarised in Table 1.

The results indicated that these complexes show in both solvents a quasi-reversible oxidation of Co (II) to Co (III). In AN solution in the used potential range they exhibit one anodic peak and the corresponding cathodic peak. The values of $E_{1/2}$ (vs. Ag/AgCl) are very similar and the anodic-cathodic peak potential separations, for the lowest scan rates used, are comparable to that of Fc⁺/Fc couple, but somewhat higher for fast sweep rates. The ratio $i_{pc} : i_{pa}$ was found to decrease with increasing scan rates.

Table 1. Cyclic voltametric data fo Co(II) complexes in Acetonirile (AN) and (CH₂Cl₂ + (CH₃)₂SO) in (0.1 M TBAP) ^a

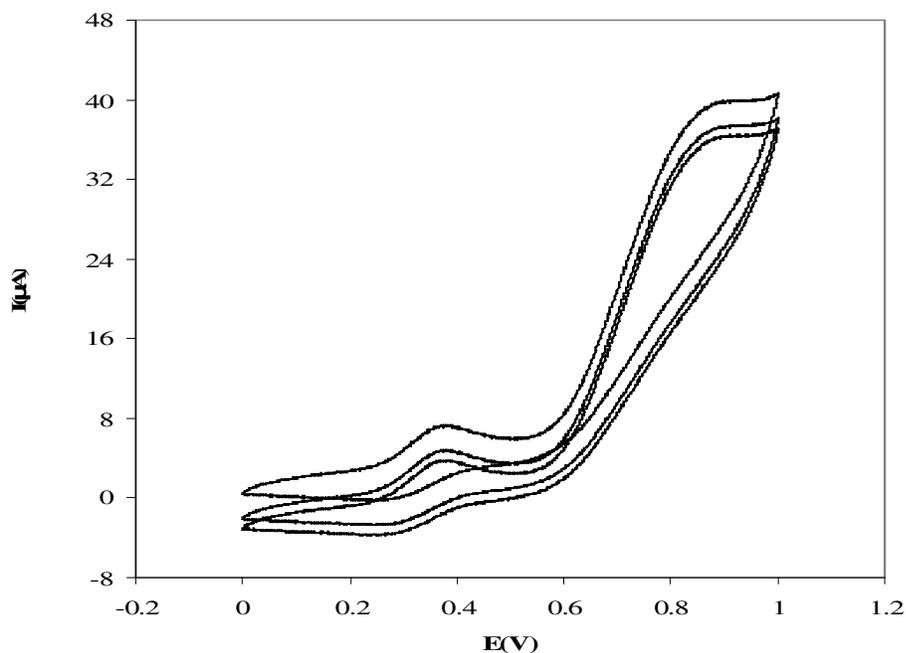
Complex	$\nu(V/s)$	In AN				In (CH ₂ Cl ₂ + (CH ₃) ₂ SO)				
		E _{pa}	E _{pc}	ΔE	$i_{pc}:i_{pa}$	E _{pa(I)}	E _{pa(II)}	E _{pc(I)}	ΔE	$i_{pc} : i_{pa}$
1	0.01	0.87	0.78	0.08	1.02	0.38	0.91	0.30	0.08	1.05
	0.50	0.92	0.73	0.19	0.68	0.5	B	0.32	0.22	0.70
2	0.01	0.85	0.78	0.07	1.02	0.37	0.88	0.30	0.07	1.03
	0.5	0.89	0.74	0.15	0.75	0.53	B	0.33	0.20	0.80
3	0.01	0.94	0.84	0.10	1.00	0.40	-	0.32	0.08	0.95
	0.5	0.94	0.85	0.09	0.97	0.59	-	0.36	0.23	0.82

1:[Co(pytaNO₂)] 2:[Co(pytaOMe)] 3:[Co(pytaBr)]

^a All potentials are referred to Ag/AgCl (3M KCl).

^b The anodic wave is not detected at high scan rates.

^c Electrochemical process with a high degree of irreversibility.

**Figure 3.** Cyclic voltammograms of [Co (PytaNO₂)] in 0.1 M TBAP– (CH₂Cl₂+(CH₃)₂SO) between -0.2 and 1.00 V at different scan rates: (i) 0.005, (ii) 0.010, (iii) 0.020.

3.3. The effect of solvent

The cyclic voltammograms of [Co (PytaoMe)], [Co (PytaNO₂)] and [Co (PytaBr)] are solvent dependent; The behaviour of [Co (PytaoMe)], [Co (PytaNO₂)] and [Co (Pyta Br)] in (CH₂Cl₂ + (CH₃)₂SO) is more intricate, since the voltammograms are dependent on scan rate. At low scan rates (0.005–0.02 V/s), two anodic waves, E_{pa}(I) and E_{pa}(II), but only one cathodic wave, which is related to the first anodic process (E_{pc}(I)), could be detected (Fig. 3 and Table 1). As the scan rate increases, a positive shift in E_{pa}(I) and E_{pa}(II) (larger for the latter process) and an increase in peak current (smaller for the latter process) are observed.

As seen in Fig. 4, for scan rates faster than 0.05 V/s only the first anodic wave and the corresponding cathodic wave could be observed.

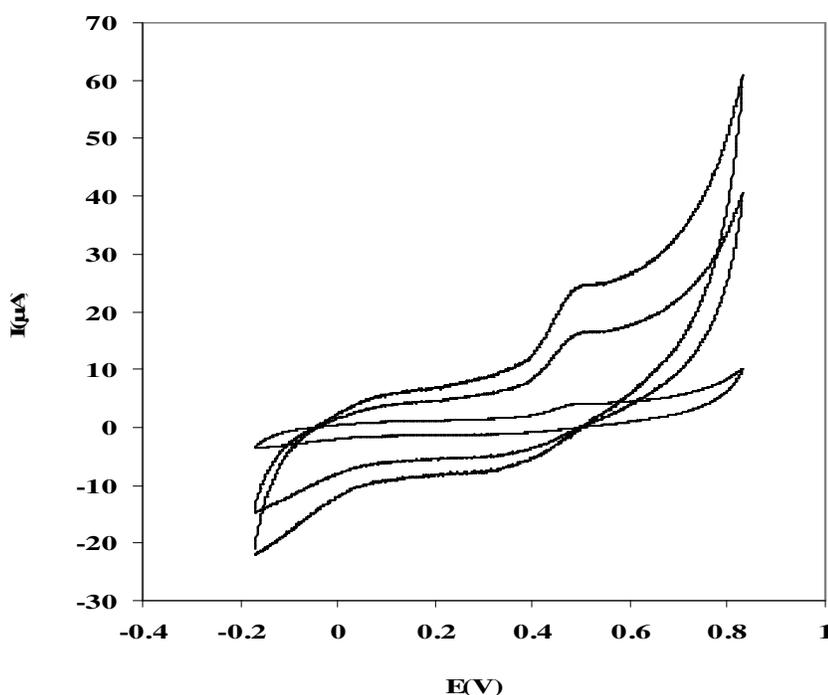


Figure 4. Cyclic voltammograms of [Co (PytaNO₂)] in 0.1 M TBAP– (CH₂Cl₂+ (CH₃)₂SO) between -0.2 and 1.00 V at different scan rates: (v) 0.100, (vi) 0.500, (vii) 1.00 V/s.

The ratio $i_{pc}:i_{pa}$ (Table 1) for the first process is somewhat larger than 1 for low scan rates, but smaller than 1 for the highest scan rates.

For [Co (PytaoMe)], [Co (PytaNO₂)] and [Co (PytaBr)] in the two solvents, the dependence of i_p with $n^{1/2}$ was found to be linear at low scan rates, but to deviate from linearity with increasing sweep rate. By coupling these results with the observations that, with increasing scan rate, the ratios $i_{pc}:i_{pa}$ become smaller than 1 and the anodic–cathodic peak potential separation (ΔE) becomes larger than the values for Fc⁺/Fc, it becomes clear that the rate of the electron transfer, relative to that of the mass transport, is insufficient to maintain the Nernstian equilibrium at the electrode surface. The one-

electron charge transfer process is thus reversible and diffusion controlled at low scan rates, whereas at high scan rates a transition to a Quasi-reversible mixed (kinetic and diffusion) controlled process must take place [23].

In both solvents the current-scan rate responses in cyclic voltammetry experiments for [Co (PytaOMe)], [Co (PytaNO₂)] and [Co (PytaBr)], depicted as i versus $v^{1/2}$ (Randles–Sevcik representation [24]), are straight lines that exhibit small deviations from linearity. These deviations from linearity suggest a change from a diffusion-controlled process to a mixed controlled process [25], as has been inferred from cyclic voltammetry in (CH₂Cl₂ + (CH₃)₂SO). By using the linear region of the Randles–Sevcik equation, the diffusion coefficients for oxidation (D_{oxi}) was calculated and are summarized in Table 2.

Table 2. Diffusion coefficient values data for Co (II) complexes in Acetonitril (AN) and (CH₂Cl₂ + (CH₃)₂SO) in (0.1 M TBAP) ^aAN,

Complex	In AN		<i>In</i> (CH ₂ CL ₂ + (CH ₃) ₂ SO)	
	$D(\text{cm}^2 / \text{s}) \times 10^{-6}$	α	$D(\text{cm}^2 / \text{s}) \times 10^{-6}$	α
1	9.20	0.66	4.00	0.62
2	8.91	0.70	3.68	0.68
3	8.35	0.67	2.98	0.70

Analysis of D shows that: (1) the values in AN are higher than those obtained in CH₂Cl₂ + (CH₃)₂SO, and (2) the value in both solvents in the order [Co (PytaNO₂)] > [Co (PytaOMe)] > [Co (PytaBr)]. Solvent dependence can easily be accounted for by differences in solvent dielectric constant [23-24]: the complexes have smaller D values in the solvent with dielectric constant, (CH₂Cl₂ + (CH₃)₂SO).

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