SYNTHESIS AND CHARACTERIZATION OF AMINE(CHLORO)COBALOXIME DERIVATIVES. APPROXIMATE VALUES OF THE ANGULAR-OVERLAP PARAMETER, σ, FOR THE COORDINATED AMINES

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Abstract

Four new complexes of the type $[LCo^{III} ((DO)(DOH) pn) Cl] PF_6$ where (DO) (DOH) pn = N^2, $N^{2\prime}$- propanediylbis (2, 3-butanedione2-imine3-oxime) and L = morpholine (mrpln) (I), benzylamine (bzlan) (II), piperidine (pprdn) (III) and pyrrolidine (prldn) (IV) have been synthesized and characterized by elemental analyses and spectroscopic methods. Approximate values of the angular-overlap parameter, σ, for the coordinated amines are estimated to be: 6395, 6627, 6797, and 7076 cm^{-1} for mrpln, bzlan, pprdn, and prldn, respectively.

Introduction

Many aspects of the chemistry of cobaloximes [1-4] have been studied extensively in recent years, with the emphasis on the electrochemical properties. The role played by the axial ligands in photochemistry [1] and electrochemical behaviour [5] of these compounds is remarkable and derivatives of Costa-type complexes with inorganic ligands have only recently been well characterized [5]. The rigidity of the tetradentate, (DO) (DOH)pn [6], equatorial ligand, prompted us to consider these complexes as good candidates for the investigation of the structural effects on the photochemical behaviour of Co(III) coordination compounds.

Herein we report the synthesis and characterization of $[(amine) Co ((DO) (DOH) pn) Cl] PF_6$ type complexes in which an axial amine ligand (I, mrpln = morpholine; II, bzlan = benzylamine; III, pprdn = piperidine; and IV, prldn = pyrrolidine) is located trans to the axial chloride ligand (Fig. 1). Approximate values for the angular-overlap parameter, σ, of the coordinated amines, which are used in rationalizing the photochemical behaviour of these complexes are also reported.

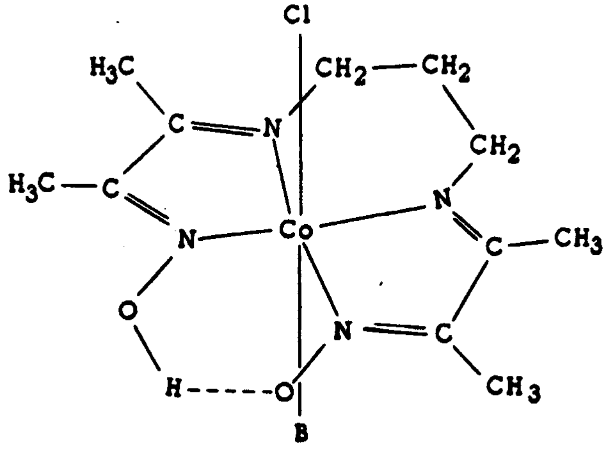

Figure 1. The structure of trans- $[BCo ((DO)(DOH) pn) Cl]^+$ complexes

Keywords: Amine(chloro)cobaloxime derivatives; A. O. parameter; Synthesis

Materials and Methods

[Co ((DO) (DOH) pn) Cl_2] was prepared as described in the literature [7]. Morpholine (mrpln), benzylamine (bzlan), piperidine (pprdn), and pyrrolidine (prldn) (Merck) were distilled under reduced pressure. All other chemicals were commercial reagent grade and used as received from Aldrich and Merck.

Physical Measurements

UV-visible absorption spectra in solution were recorded with a Shimadzu UV-240 spectrophotometer. IR spectra were recorded as KBr pellets on a Shimadzu 435 IR spectrophotometer. ^1H NMR spectra were obtained on a Varian EM-390 90MHz NMR spectrometer. Proton chemical shifts were referenced to TMS. Elemental analyses were performed by using a Haraeus CHN-O-RAPID elemental analyzer.

Synthesis of [(mrpln)Co((DO)(DOH) pn)Cl]PF_6 (I)

To a stirring solution of [Co ((DO) (DOH) pn) Cl_2], [7] (2.0 g, 5.4 mmol) in acetonitrile (200 ml) was added a solution of KPF_6 (1.7 g, 9.24 mmol) in acetonitrile (60 ml), followed by morpholine (0.47 ml, 5.4 mmol), and the reaction mixture was stirred for 1 h at room temperature. The resulting red solution was filtered off in order to remove the white precipitate, KCl. The filtrate was then transferred to a 500 ml round-bottom flask and the solvent was removed on a rotary evaporator (45°C). The red solid residue was treated with 100 ml of acetonitrile and filtered off, and 40 ml of 1,4-dioxan was added to the filtrate. The final solution was allowed to stand undisturbed in the hood at room temperature. After 2 days, red crystals of [(mrpln) Co((DO)(DOH)pn) Cl]PF_6 were isolated by filtration and washed with a 30 ml mixture of acetonitrile- dioxan (1: 5 v/v) and dried in vacuo. Yield 1.28 g (42%). ^1H NMR (DMSO-d_6, ppm): 18.80 (1H, s), 4.35 (4H, m), 3.68 (4H, t), 3.00 (4 H, t), 2.80 (1H, s), 2.60 (6H, s), 2.50 (6H, s), 1.55 (2H, m).

Synthesis of [(bzlan)Co((DO)(DOH)pn)Cl]PF_6 (II)

This complex was prepared by a procedure similar to that for (I) except that benzylamine (0.59 ml, 5.4 mmol) was used as the amine ligand. Yield 1.46 g (46%). ^1HNMR (DMSO-d_6, ppm): 18.82 (1H, s), 7.45 (5H, m), 4.35 (4H + 2H, m), 2.60 (6H, s), 2.48 (6H, s), 2.40 (2H, s), 1.55 (2H, m).

Synthesis of [(pprdn)Co((DO)(DOH)pn)Cl]PF_6 (III)

This complex was prepared by a procedure similar to that for (I) except that piperidine (0.54 ml, 5.4 mmol) was used as the amine ligand. Yield 1.55 g (51%). ^1H NMR (DMSO - d_6, ppm) : 18. 86 (1H, s), 4. 35 (4H, m), 3.20 (1H, s), 2.85 (4H, t), 2.6 (6H, s), 2.51 (6H, s), 1.55 (6H + 2H, m).

Synthesis of [(prldn)Co((DO)(DOH)pn)Cl]PF_6 (IV)

This complex was prepared by a procedure similar to that for (I) except that pyrrolidine (0.45 ml, 5.4 mmol) was used as the amine ligand. Yield 1.28 g (42%). ^1H NMR (DMSO-d_6, ppm): 18. 90 (1H, s), 4.35 (4H, m), 3.25 (1H, s), 2.82 (4H, t), 2.62 (6H, s), 2.51 (6H, s), 1.70 (4H+ 2H, m).

Results and Discussion

Preparation of trans- [(amine) Co ((DO) (DOH) pn) Cl] PF_6 complexes I-IV, in aqueous media, which has been reported for the synthesis of similar trans-(chloro) (pyridine) compounds [5], proved to be unsuccessful. This is apparently due to the fact that the amine ligands used in this work are stronger bases relative to pyridine (pK_a = 11.27, 11.123, 9.33, 8.33 and 5.25 for prldn, pprdn, bzlan, mrpln, and py, respectively [8]), and may result in the hydrolysis of the starting material in aqueous solution.

The red crystals of these complexes are thermally stable up to 190°C and they give stable solutions in polar solvents such as DMSO, and acetonitrile. However, when dissolved in water, these complexes undergo a very slow hydrolysis. Some physical properties and analytical data of the compounds are listed in Table 1.

^1H NMR spectral data of compounds I-IV were collected in DMSO-d_6, and relevant chemical shifts of the O–H...O signals, and equatorial methyl signals are reported in Table 2. The dichloro and (chloro) (pyridine) complexes are also included [5] for comparison. The overall patterns of the ^1H NMR spectra of the compounds are similar to those of the references. The variation of the O–H...O signal is in accord with the inductive effect of the coordinated amines.

The IR spectra of I-IV show similar absorption patterns in 2500-400 cm^{-1} region indicating the existence of (DO) (DOH) pn as the common equatorial ligand [9] and PF_6^- as the counterion [10]. The most important feature of the IR spectra in 4000-2500 cm^{-1} region is the N-H stretching vibration of the coordinated amines and the O-H stretching vibration of the equatorial ligand (Fig. 2). A medium band for the N-H stretching vibration of the coordinated secondary amine [11] is observed at 3155, 3172, and 3168 cm^{-1} for morpholine, piperidine, and pyrrolidine complexes, respectively. For the benzylamine complex, two medium bands at 3025 and 3150 cm^{-1} are observed which is in agreement with the coordination of a primary amine [11]. The O–H stretching vibration of the equatorial ligand appears at about 2900 cm^{-1} for all four complexes, however, since the C–H stretching bands, (at 2800-2900 cm^{-1}), interfere with this band, the O–H stretching is not easily discernible.

The electronic absorption spectra of I-IV along with

Table 1. Physical properties and analytical data

No.	Complex*	Color	(m. p. °C)	Found (Calc). %		
				C	H	N
I	[(mrpln) CoLCl] PF_6 $(CoC_{15}H_{28}ClF_6N_5O_3P)$	Red	193 (d)	32.10 (31. 84)	5.10 (5. 00)	12.40 (12. 38)
II	[(bzlan) CoLCl] PF_6 $(CoC_{18}H_{28}ClF_6N_5O_2P)$	Red	212 (d)	37.20 (36.96)	4.80 (4.82)	12.10 (11.96)
III	[(pprdn) CoLCl]PF_6 $(CoC_{16}H_{30}ClF_6N_5O_2P)$	Red	201 (d)	33.80 (34.08)	5.30 (5.36)	12.30 (12.42)
IV	[(prldn)CoLCl]PF_6 $(CoC_{15}H_{28}ClF_6N_5O_2P)$	Red	196 (d)	32.60 (32.77)	5.20 (5.13)	12.60 (12.74)

* L = ((DO) (DOH) pn)
d = melts with decomposition

Table 2. Selected ^{1}H NMR chemical shifts for I-IV[a]

No.	Complex*	O—H...O	$C-N=C-CH_3$	$O-N=C-H_3$
I	[(mrpln) CoLCl] PF_6	18.80	2.60	2.50
II	[(bzlan) CoLCl] PF_6	18.82	2.60	2.48
III	[(pprdn) CoLCl]PF_6	18.86	2.60	2.51
IV	[(prldn)CoLCl]PF_6	18.90	2.62	2.51
	[(py) CoLCl]PF_6[b]	18.80	2.59	2.50
	$CoLCl_2$[b]	19.40	2.58	2.51

* L = ((DO) (DOH) pn)
[a] =Chemical shift in ppm relative to TMS in DMSO-d_6
[b] Ref.5

the dichloro complex in CH_3CN are shown in Figure 3, and the spectral data are summarized in Table 3. A broad band observed in the visible region of the spectrum for all four complexes can be attributed to the first ligand field transition, $^1A_{1g} \rightarrow {}^1T_{1g}(^1Eg, {}^1A_{2g})$, of these low spin d^6 complexes [12]. Although the reduction of symmetry from O_h to D_{4h}, (i.e. the effective holohedron symmetry for I-IV), does produce an additional splitting, the effect is small. The second ligand field transition is hidden under the very intense charge-transfer band.

The energy of the first absorption band, along with the data from the state correlation diagram [13] for D_{4h}, presented in Figure 4, were used to estimate the approximate value of the angular overlap parameter, σ, for the coordinated amines. The energies of the ground and the first excited state of these D_{4h} complexes are presented by equations 1 and 2, respectively [13]:

$$E\,(^1A_{1g}) = 15A - 30B + 15C - 24Dq + 14Dt \qquad (1)$$

$$E\,(^1E_g) = 15A - 30B + 14C - 14Dq + (21/4)Dt \qquad (2)$$

Using equations 1 and 2, the energy of the first transition is given by:

$$E_{LF} = E\,(^1E_g) - E\,(^1A_{1g}) = 10Dq - (35/4)Dt - C \qquad (3)$$

where Dt, the tetragonal parameter [12], is defined as:

$$Dt = (-6/35)\delta_\sigma + (8/35)\delta_\pi \qquad (4)$$

Substituting for $\delta_\sigma = \sigma_{ax} - \sigma eq$, and $\delta_\pi = \pi_{ax} - \pi_{eq}$ in equation 4 and then Dt in equation 3, one obtains:

$$E_{LF} = 10Dq + 1/2\,[3\,(\sigma_{ax} - \sigma_{eq}) + 4(\pi_{eq} - \pi_{ax})] - C \qquad (5)$$

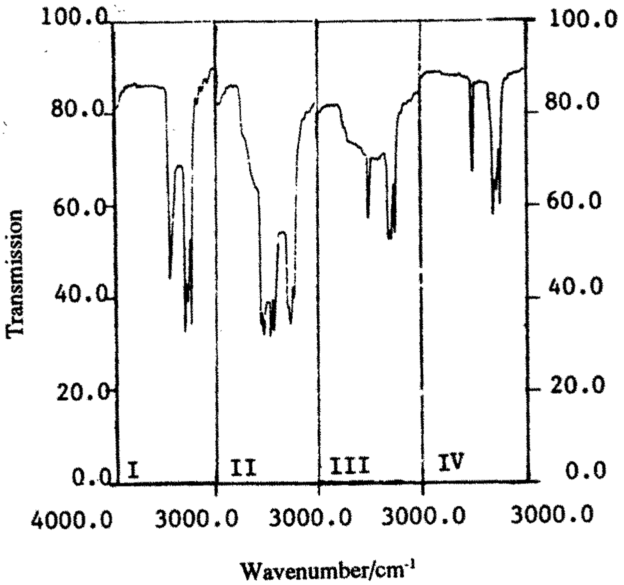

Figure 2. The 4000-2500 cm^{-1} region of infrared spectra of trans [(amine) Co((DO)(DOH)pn) Cl] PF_6 complexes, I-IV

Table 3. Electronic spectral data* and AO parameter, σ_{amine}

Complex	Electronic transition^a	LF and AO parameters^b	
	$^1A_{1g} \rightarrow {}^1T_{1g}$ (^1E_g,$^1A_{2g}$)	10Dq	σ
I	495 (707)	19185	6395
II	489 (656)	19881	6627
III	481 (631)	20389	6797
IV	475 (623)	21227	7076
$CoLCl_2$^{c}	558 (41)	13710	6290

* All spectra obtained in CH_3CN

^{a} λmax values in nm; ε values in parentheses in $M^{-1}cm^{-1}$

^{b} In cm^{-1}; ^{c}$CoLCl_2$ = Co((DO)(DOH)pn)Cl_2 (Ref. 5,14).

Using equation 5, the energies of the first absorption bands for trans- [$CoLCl_2$], A, and trans-[CoL (amine) Cl] PF_6, B, complexes {where L= ((DO)(DOH)pn)}, are calculated to be:

$$E_{LF}(A)=4/6(10Dq)_L + 2/6(10Dq)_{Cl} + 1/2\ [3\ (\sigma_{Cl} - \sigma_L) + 4(\pi_L - \pi_{Cl})] - C \qquad (6)$$

$$E_{LF}(B) = 4/6(10Dq)_L + 1/6\ (10Dq)_{Cl} + 1/6\ \ (10Dq)_{amine} + 1/2\ \{3\ [1/2\ (\sigma_{Cl} + \sigma_{amine}) - \sigma_L] + 4[\pi_L - 1/2\ (\pi_{Cl} + \pi_{amine})]\} - C \qquad (7)$$

$$\Delta E_{LF} = E_{LF}(B) - E_{LF}(A) = 1/6\ [(10Dq)_{amine} - (10Dq)_{Cl}] - 3/4\ [\sigma_{Cl} - \sigma_{amine}] + \pi_{Cl} \qquad (8)$$

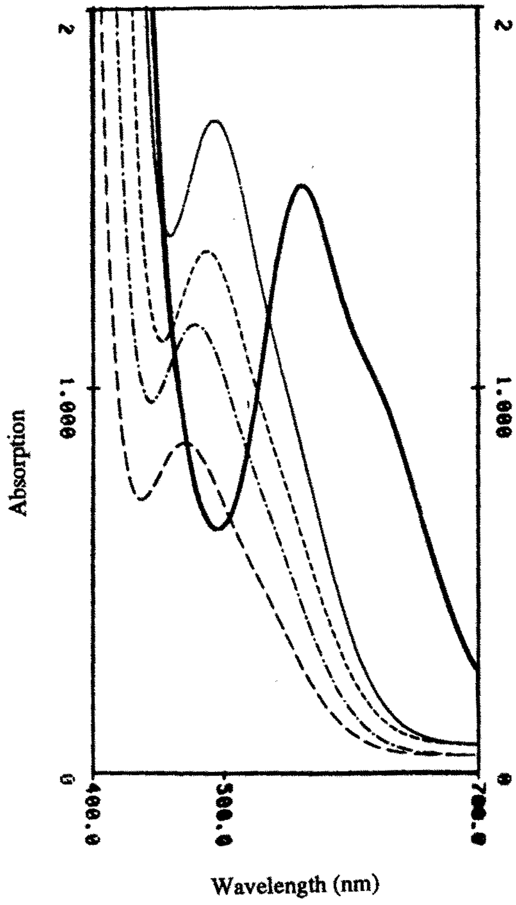

Figure 3. Visible absorption spectra of I (——), 2.40×10^{-3}M; II (---), 2.07 × 10^{-3}M; III (-.-.-), 1.84 × 10^{-3}M; IV (___), 1.36 × 10^{-3}M; and $CoLCl_2$ (——), 3.70 × 10^{-2} M, (Ref 5); in CH_3CN at 25°C

Substituting for 10Dq= 3σ - 4π, one obtains:

$$\Delta E_{LF}(cm^{-1}) = 10^7\ [(1/\lambda_B) - (1/\lambda_A) = 5/12(3\sigma_{amine} - 3\sigma_{Cl} + 4\pi_{Cl}) \\ = 5/12(3\sigma_{amine} - 10Dq_{Cl}) \qquad (9)$$

A sample calculation for morpholine complex (λ_{max} = 495 nm), (Table 3), using $10Dq_{Cl}$ = 13710 cm^{-1} [14], is presented:

$$\Delta E\ (cm^{-1}) = 10^7\ (1/495 - 1/558) = 5/12(3\sigma_{mrpln} - 13710) \\ \therefore \sigma_{mrpln} = 6395 cm^{-1} \qquad (10)$$

The calculated σ values for the coordinated amines, using equation 9, are given in Table 3.

As is expected, the estimated σ values are in accord with the donorability of the amine ligands. These values are of key importance [15, 16] in rationalizing the

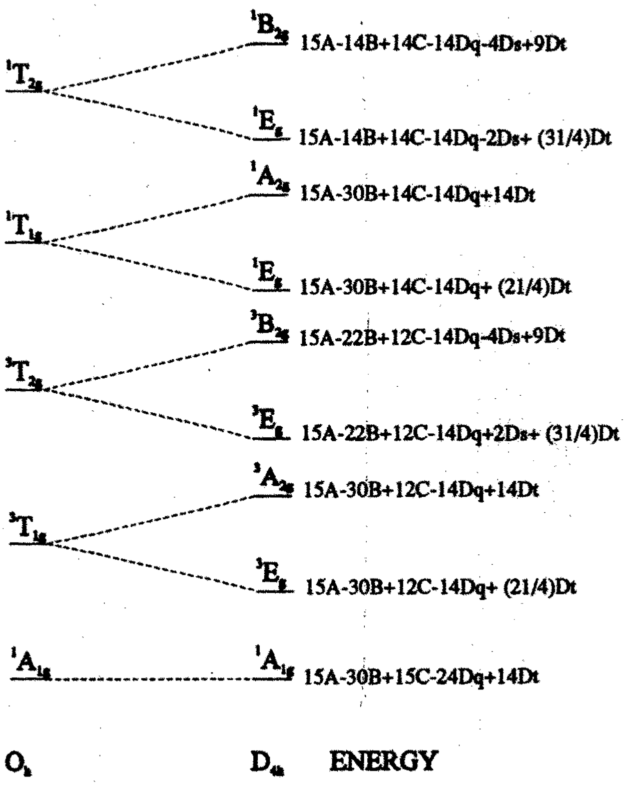

Figure 4. The state correlation diagram between an O_h low spin d^6 complex and the tetragonally distorted D_{4h}

photochemical behaviour of trans - [(amine) Co ((DO)(DOH) pn) Cl]$^+$ complexes in the ligand field region which is currently under way in our laboratory.

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