

Magnetic and Spectral Properties of some Cobalt(II) Complexes of Vitamin B₁

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Abstract

Some cobalt(II) complexes of vitamin B₁ and its derivatives have been prepared and characterised by elemental analysis, IR and electronic spectra, conductivity and magnetic susceptibility measurements. One of the new complexes, Co(Th)Br₃·H₂O is found to be isomorphous with the Co(Th)Cl₃ analogue already reported [1], as both exhibit identical IR spectra. Although, the thiocyanato complex, [Co(Th)(OAc)SCN]SCN also assumes a tetrahedral structure, it is found to be a 1:1 electrolyte in nitromethane. The iodo complex, on the other hand, assumes a distorted square pyramidal structure and it is only partially ionised in the same solvent.

The relative stability of these complexes has been put roughly as Cl > Br > SCN > I based on the shift of the $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})$ modes of the complexes relative to the respective ligands, and on the decomposition temperatures of the complexes.

Introduction

We recently reported [1] the preparation and some properties of Co(Th)Cl₃, the first cobalt(II)

complex of vitamin B₁ in which there is direct metal–ligand bonding. In order to establish the possible effect of anions on the stoichiometry, stereochemistry and stability of these cobalt(II) complexes, we have prepared more cobalt(II) complexes in the hope that any difference in the magnetic and spectral properties of these complexes should be due to the different groups in the coordination sphere of the cobalt ion.

Experimental

Physical Measurements

Elemental analyses were performed by the micro-analytical laboratories of the University of Ibadan and University College, Dublin. Cobalt was estimated complexometrically using the standard method. Melting points were determined using a Gallenkamp melting point apparatus. The analytical results along with the colours and melting points are presented in Table 1. The IR spectra were recorded on a Perkin-Elmer 457 grating infrared spectrophotometer in the range 4000–200 cm⁻¹, using pressed KBr discs and nujol mulls. The diffuse reflectance electronic spectra were measured in the range 335–1000 nm on a SP500 spectrophotometer using CaCO₃ as a reference. The magnetic susceptibility measurements were

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TABLE 1. Colour, melting point and analytical data for the cobalt(II) complexes

Compound	Colour	Melting point (°C)	Analysis: found (calc.) (%)				μ_{eff} (BM)	Λ_{m} (ohm ⁻¹ cm ⁻² mol ⁻¹ ; 10 ⁻³ M)	
			C	H	N	Metal		CH ₃ NO ₂	DMF
Co(Th)Cl ₃	blue	212–213	33.39 (33.46)	3.98 (3.95)	12.98 (13.01)	13.72 (13.68)	4.72	15	15
Co(Th)Br ₃ ·H ₂ O	blue	168	24.73 (24.76)	3.17 (3.27)	8.62 (9.62)	10.51 (10.13)	4.82	9.8	156.8
[Co(Th)(OAc)SCN]SCN	deep blue	177	37.87 (38.41)	3.76 (4.04)	16.44 (16.82)	11.78 (11.80)	4.54	85	129.5
[Co(Th)(OAc) ₂]I	light pink	160	33.21 (33.73)	3.10 (2.97)	9.78 (9.89)	10.46 (10.34)	4.24	48	72

carried out at room temperature using a Johnson Matthey magnetic susceptibility balance.

The samples were free from ferromagnetic impurities and the diamagnetic corrections were calculated from tables of Pascal's constants.

Preparation of Vitamin B₁ Derivatives

The bromo, iodo and thiocyanato derivatives of thiamin Th·HX₂ (X = Br, I or SCN) were prepared by reacting Th·HCl₂ with either the sodium or potassium salt of X (1:5 molar ratio) in warm aqueous medium and recrystallising the product from hot water.

Preparation of the Complexes

Co(Th)Cl₃ was prepared employing the method outlined in our earlier paper [1].

The new complexes were prepared by mixing 0.01 mol of cobalt(II) acetate tetrahydrate, suspended in 50 cm³ methanol and 0.01 mol of the respective ligands suspended in 100 cm³ methanol over a period of 15 min with constant stirring at room temperature. The reaction mixtures were kept stirring for 3 h. The solid products formed by the thiocyanato and iodo complexes were filtered by suction, washed with hot methanol, acetone and ether. In the case of the bromo complex no solid product was formed. The reaction mixture was filtered and the filtrate treated with ether whereby an intense blue complex was

precipitated. The product was filtered and washed with methanol and acetone and dried in a drying pistol under vacuum over P₂O₅ at room temperature. The other two complexes were air-dried overnight and then in the oven at 100 °C for 3 h.

Results and Discussion

The chloro, bromo and thiocyanato complexes have a blue colour which is characteristic of tetrahedral stereochemistry for cobalt(II) complexes. The iodo complex, on the other hand, is light pink, suggesting a different stereochemistry. The order of thermal stability is Cl > SCN > Br > I. This order relates roughly to the increase in the degree of polarisability of the anions (Cl < Br < SCN < I) and the π-character of the M–X bond (SCN and I are π-bonding). The Co(Th)Cl₃ and Co(Th)Br₃·H₂O are non-electrolytes while [Co(Th)(OAc)(SCN)]SCN and probably [Co(Th)(OAc)₂]I are 1:1 electrolytes in nitromethane. In dimethylformamide, however, the chloro is a non-electrolyte while the Co(Th)Br₃·H₂O and [Co(Th)(OAc)SCN]SCN are 1:2 electrolytes, and [Co(Th)(OAc)₂]I is a 1:1 electrolyte (Table 1).

Infrared Spectra

The relevant IR data of thiamin and the cobalt(II) complexes are presented in Table 2. The major bands have been assigned in our preliminary report [1].

TABLE 2. Some relevant infrared frequencies for thiamine HCl₂ and the cobalt(II) complexes^a

Thiamin·HCl ₂	CoThCl ₃	CoThBr ₃ ·H ₂ O	[CoTh(OAc)SCN]SCN	[CoTh(OAc) ₂]I	Tentative assignment
3450vs	3452vs	3460vs	3440vs	3440–3080br	OH, NH ₂ and CH (aromatic or aliphatic)
3435vs	3414vs	3410vs	3366s		
3270vs	3331vs	3330s	3320s		ν(CN)
	3234vs	3230s	3291s		
1658vs	3089vs	3080s	3188vs	1650–1630br	ν(C=O) NH ₂ bending + ring stretching coupling
			2088vs		
			2067vs		
			1682s		
1608vs	1644vs	1640vs	1652w		
	1614vs	1605vs	1617s	1555m	ν(C=C) + ν(C=N) for complexes
	1593sh	1585m	1553m		
1552s	1545m	1505m			
1538s	1505sh	1542m	1538s	1541s	ν(C=C) + ν(C=N) for respective ligands
		1502w	1508sh	1503m	
1035vs	1075s	1075s	1060s	1055s	δ(OH)
	1040m		824m		ν(CS)
			787m		
	521s	548w	543w	549w	νCo–N(pyrimidine)
		356w		390w	ν(Co–O)
	309s	322m			ν(Co–X)

^avs = very strong; s = strong; m = medium; w = weak; sh = shoulder; br = broad.

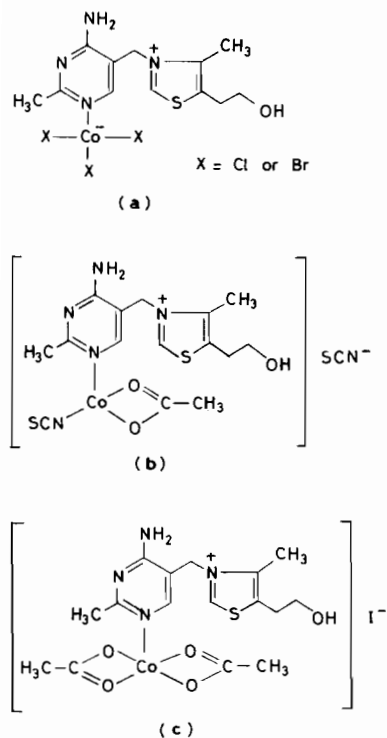


Fig. 1. Proposed structures of the cobalt–thiamin complexes.

The $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})$ modes located at 1533 and 1507, 1542 and 1502, 1538 and 1508, and 1541 and 1503 cm^{-1} in the ligands shifted to 1593 and 1552, 1585 and 1545, 1553 and 1505, and 1555 cm^{-1} in the chloro, bromo, thiocyanato and iodo complexes respectively.

The shift in the $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})$ modes in all the complexes relative to the ligands is indicative of coordination via the ring nitrogen [1]. This shift is in the order $\text{Cl} > \text{Br} > \text{SCN} > \text{I}$. To a first approximation it is believed that the greater the shift in the $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})$ modes, the stronger the Co–N bond hence the stability order of these complexes could be put as $\text{Cl} > \text{Br} > \text{SCN} > \text{I}$. The apparent irregularity when compared with either the order of thermal stability or the order of $\nu(\text{Co}–\text{N})$ (see below) is probably due to structural differences (Fig. 1). The appearance of the $\delta(\text{OH})$ mode in all the complexes precludes the OH group from being involved in coordination, although a change in the position of the OH band occurs in all the complexes relative to the ligands. This shift may be a consequence of hydrogen bonding. The weak band at 521, 548, 543 and 549 cm^{-1} in the chloro, bromo, thiocyanato and iodo complexes, respectively is unambiguously assigned to the Co–N(pyrimidine) band since this is conspicuously absent in the ligand. Unexpectedly though, the order of the $\nu(\text{Co}–\text{N})$ frequencies is in reverse order to the shifts observed in $\nu(\text{C}=\text{C}) + \nu(\text{C}=\text{N})$ for which we cannot provide an explanation. Another evidence

for complexation is reflected in the medium bands at 309 and 322 cm^{-1} for the chloro and bromo complexes, respectively. In thiocyanato complex the band at around 2000 cm^{-1} is ascribed to the $\nu(\text{CN})$ mode. Aside from the fact that this band is absent in the chloro, bromo and iodo complexes, it is split into two at 2088 and 2067 cm^{-1} . This observation [2] may either be due to the bridging structure (M–NCS–M) where the metal is bound to both the N and S donor atoms simultaneously or to the fact that there are two types of SCN group: one in the primary coordination sphere and the other in the secondary coordination sphere. Another interesting feature of the thiocyanato complex is the presence of a strong band at 1682 cm^{-1} which is unambiguously ascribed to the $\nu(\text{C}=\text{O})$ mode of the acetate group. The bands at 824 and 787 cm^{-1} are attributed to the $\nu(\text{CS})$ mode while the weak and broad band at 410 cm^{-1} is due to the $\nu(\text{Co}–\text{O})$ mode. In the case of the iodo complex a broad band is observed at 1650–1630 cm^{-1} which is ascribed to the $\nu(\text{C}=\text{O})$ of the acetate group overlapping with NH_2 bending and ring stretching coupling. The weak band at 390 cm^{-1} is due to the $\nu(\text{Co}–\text{O})$ mode while the band at 658 cm^{-1} is due to the $\nu(\text{C}–\text{N})$ mode. The absence of any band assignable to Co–I is consistent with the conductivity and magnetic susceptibility (see later) data.

Electronic Spectra

The diffuse reflectance spectral data are presented in Table 3. The cobalt(II) appears to be in a tetrahedral or pseudo-tetrahedral environment in $\text{Co}(\text{Th})\text{Cl}_3$, $\text{Co}(\text{Th})\text{Br}_3 \cdot \text{H}_2\text{O}$ and $[\text{Co}(\text{Th})(\text{OAc})\text{SCN}]\text{SCN}$. The electronic spectra of the tetrahedral and pseudo-tetrahedral complexes are similar [3]. Tetrahedral cobalt(II) exhibits three spin-allowed electronic transitions to the excited quartet states: ${}^4\text{A}_2(\text{F}) > {}^4\text{T}_2(\text{F})$, ${}^4\text{A}_2(\text{F}) > {}^4\text{T}_1(\text{F})$ and ${}^4\text{A}_2(\text{F}) > {}^4\text{T}_1(\text{P})$.

In $\text{Co}(\text{Th})\text{Cl}_3$ and $\text{Co}(\text{Th})\text{Br}_3 \cdot \text{H}_2\text{O}$ complexes, the bands in the range 15–16.4 kK have been assigned to the ${}^4\text{A}_2(\text{F}) > {}^4\text{T}_1(\text{P})$ transition while the broad band around 10.2 kK is assigned to the ${}^4\text{A}_2(\text{F}) > {}^4\text{T}_1(\text{F})$ transition. The low intensity bands in the range 17.5–23.8 kK in those complexes is probably due to spin-forbidden transition [4].

$[\text{CoTh}(\text{OAc})_2]\text{I}$ exhibits different spectral properties. Evidence from other measurements indicate that this complex is most likely to be five-coordinate and therefore should have either a square pyramidal or trigonal bipyramidal geometry. Trigonal bipyramidal complexes of Co(II) are characterised by a band in the near IR region, from 5000–8000 (${}^4\text{A}_2 > {}^4\text{E}$ in D_{3h}), a second one at 10000–13000 and two more intense bands at 16000 (${}^4\text{A}'_2 > {}^4\text{E}''(\text{P})$) cm^{-1} respectively [5]. On the other hand genuine square pyramidal Co(II) complexes, which are best regarded as analogues of the tetragonally distorted six-coordinate Co(II) with a very weak axial field [6], are

TABLE 3. Electronic spectral data of the cobalt(II) complexes

Compound	Solvent	Band	Maxima	(cm ⁻¹)			
Co(Th)Cl ₃	solid		23810	19608	16393	15873(main)	
	CH ₃ NO ₂	26641	22222		16393	14707	
	DMF	25000		19500	18000	14705	10500
Co(Th)Br ₃ ·H ₂ O	solid			18868	16393	15150(main)	
	CH ₃ NO ₂	26316	20619			14706	
	DMF	25000	20000	18182		14493	10417
[Co(Th)(OAc)SCN]SCN	solid		20833(sh) ^a	17391(main)	16129(sh)		
	CH ₃ NO ₂	26667	19802		15873	13605	10526
	DMF	25000	20408		15873	12821	11628
						12048	10989
[Co(Th)(OAc) ₂]I	solid		21277(main)	18182	17544	14492(sh)	
	CH ₃ NO ₂	26316			16393	14152	11236
	DMF	24390			15625	13699	10638
						11364	10417

^ash = shoulder.

relatively rare [7, 8]. In the few reported cases three bands are generally observed in the visible region at about 11 000, 17 000 and 20 000 cm⁻¹. Bands corresponding to these ones in the iodo complex are observed at ~10.5–11.4, 16.4–18.1, and ~21.3 kK respectively. Although the gross spectra of square pyramidal Co(II) complexes do not differ markedly from high-spin trigonal bipyramidal species [6] the occurrence of the most intense band at ~21.3 kK (and not at about 16.0 kK), coupled with the magnetic and conductivity data tend to lend stronger support to the iodo complex having a square pyramidal geometry, with the probability of some distortion.

The solution spectra of all complexes in nitromethane and dimethylformamide are similar to the diffuse reflectance spectra.

Magnetic Susceptibility

The room temperature magnetic moments of the complexes are given in Table 1. The magnetic moments of Co(Th)Cl₃, Co(Th)Br₃·H₂O, [Co(Th)(OAc)SCN]SCN and [CoTh(OAc)₂]I are 4.67, 4.82, 4.54 and 4.28 BM, respectively, indicating three unpaired electrons. While the moments for the chloro, bromo and thiocyanato complexes are in agreement with values expected for tetrahedral cobalt(II) complexes [9] it seems that the moment for the iodo complex may be better rationalised if a square pyramidal or trigonal bipyramidal structure is assumed [10]. In the absence of any suitable

crystals for X-ray analysis, we propose the following structures (Fig. 1) which are believed to be consistent with the above data. We must add, however, that in the case of (b) and (c) SCN⁻ and I⁻ can be part of the ligand molecules, next to the thiazolium N⁺.

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