PHYSICOCHEMICAL AND ANTIMICROBIALPROPERTIES OF SOME COBALT(II) COMPLEXES

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ABSTRACT

Mixed halides and nitrate cobalt(II) complexes of the type $[CoXLY_2]^{2-}$, $[CoX_2LY]^{2-}$ (where X and L are different halides and Y = nitrate) have been synthesised. The crystal field parameters, i.r, and magnetic data of the complexes suggest a tetrahedral environment of the ligating atoms around the central Co(II) ion. The antimicrobial activity if these compounds against four bacteria and a yeast is studied, and the activity compared with that of a Cobalt(II) Chloride.

INTRODUCTION

Though structural and spectral properties of regular and pseudotetrahedral Co(II) complexes of the $[CoX_4]^{2-}$ (where X = halide(1-3) and $[CoL_2(NO_3)2]$ (where L = amino (4) and Ph_3PO (5) have been reported, not much is known particularly about the structure and antimicrobial properties of mixed halides and nitrate groups in 1:1:2, 1:2:1 and 2:1:1 combinations.

Cotton and Bergman (6) have demonstrated from X-ray crystal structure of the $[Co(NO_3)_4]^{2-}$ anion that each nitrate ion is bidentate giving an eight coordination in a dodecahedral complex with the centres of the nitrate ions (N atoms) lying at the vertices of a flattened tetrahedron.

In this work the complexes of the type $[CoXLY_2]^{2-}$, $[CoXL_2Y]^{2-}$ and $[CoX_2LY]^{2-}$ (where X = halide, L = halide different from X, and Y = nitrate) have been studied, in order to compare their properties with the corresponding $[CoX_2L_2]^{2-}$, $[CoX_2Y_2]^{2-}$ species, and also the antimicrobial activity of the cobalt complexes has been compared with that of Cobalt(II) chloride, which has been reported to show such activity(7).

EXPERIMENTAL

The complexes are of the general formulae $Q_2[CoX_2L_2]$, $Q_2[CoXLY_2]$, $Q_2[CoXL_2Y]$ and $Q_2[CoX_2LY]$ where Q = Et_4N^+ ion, X and L are two different halides (e.g. Cl^-, Br^-, I^-) and Y = $NO3^-$. In all cases, the quarternary ammonium salts (TAC) and the simple Co(II) salts in the desired ratios were separately dissolved in a minimum of 1:1 acetonitrile/95% methanol solutions. The quarternary salt solutions were then gradually introduced dropwise into the Co(II) salt solutions while stirring for one hour after which the complexes were allowed to dry in vacuo over P_2O_5. The elemental analyses were carried out in the Microanalytical laboratories at the University of Ibadan (and the results are summarized in Table 1.).

The i.r spectra were recorded on a Perkin-Elmer model IR - 137 spectrophotometer using nujol and hexachlorobutadiene mulls whilst the electronic spectra in methanol solution (10^{-2} - 1.0M) were measured on a Perkin-Elmer model UV-VIS 137 and the molar extinction coefficient values were cross-checked using an SP-500 spectrophotometer. The magnetic moments were

TABLE 1: PHYSICAL AND ANALYTICAL DATA

Sample	Compound	Colour	Decomp. temp. oC	Calcd. %C	Found %C	Calcd. %H	Found %H	Calcd %Co	Found %Co	ueff B.M. 303K
1	$[(C_2H_5)_4N]_2[CoCl_2 I_2]$	Green	258-260	29.83	29.32	6.26	6.39	9.15	9.10	4.03
2	$[(C_2H_5)_4N]_2[CoCl_2Br_2]$	Green	286-288	34.93	34.82	7.33	7.30	10.71	10.40	4.08
3	$[(C_2H_5)_4N]_2[CoBr_2I_2]$	Green	> 290	26.22	26.20	5.50	5.50	8.04	8.00	4.05
4	$[(C_2H_5)_4N]_2[CoCl_2(ONO_2)_2]$	Blue	288-290	37.36	37.36	7.84	7.84	11.46	11.46	-
5	$[(C_2H_5)_4N]_2[CoI_2(ONO_2)_2]$	Dk Blue	198-200	27.56	27.23	5.78	5.37	8.45	8.39	-
6	$[(C_2H_5)_4N]_2[CoBr_2(ONO_2)_2]$	Blue	248-250	31.86	31.67	6.68	6.90	9.77	9.73	-
7	$[(C_2H_5)_4N]_2[CoBrCl(ONO_2)_2]$	Blue	246-248	34.39	33.93	7.22	7.30	10.55	10.55	-
8	$[(C_2H_5)_4N]_2[CoClI(ONO_2)_2]$	Dk Blue	200-202	31.72	31.72	6.66	6.64	9.73	9.70	-
9	$[(C_2H_5)_4N]_2[CoCl_2I_{(ONO2)}]$	Dk Blue	218-220	33.18	33.18	6.96	6.94	10.17	10.10	-
10	$[(C_2H_5)_4N]_2[CoCl_2Br(ONO_2)]$	Blue	> 250	36.11	35.99	7.58	7.70	11.07	10.93	4.06
11	$[(C_2H_5)_4N]_2[CoBrI(ONO_2)_2]$	Blue	220-222	29.55	29.52	6.20	6.20	9.06	8.99	4.04

* Compounds 4-9 are very hygroscopic.

TABLE 2: INFRARED SPECTRA - MONODENTATE ONO_2^- (C2V) (cm^{-1})

Sample	Complex						
4	$[CoCl_2(ONO_2)_2]^{2-}$	-	1026	1333	796	2387	
5	$[CoI_2(ONO_2)_2]^{2-}$	1274	1000	1333 1504	778	2381	
6	$[CoBr_2(ONO_2)_2]^{2-}$	1274	1000 1020	1326 1428	784	-	-
7	$[CoBrCl(ONO_2)_2]^{2-}$	1274	1000 1015	1429	787	-	-
8	$[CoCII(ONO_2)_2]^{2-}$	-	1000 1020	1325 1425	787	-	2083
11	$[CoBrI(ONO_2)_2]^{2-}$	-	1000 1024	1333 1428	787	-	-

determined on a Gouy balance at 303K using $Hg[Co(SCN)_4]$ as a calibrant.

Antimicrobial Ativity

The agar diffusion method which involves seeding agar with microbial suspension was employed(7) 0.5mg/ml aqueous solutions of the cobalt complexes, cobalt(II) chloride, tetraethyl ammonium chloride (TAC) and dodecyl dimethylbenxyl ammonium chloride (positive control) (QAC) were prepared in sterile water.

The Test organisms consisted of four bacterial species. *E.coli* NCTC 1093, *Staph, aureus* H484, *Pseudomnas aeruginosa* UCH 45, all grown and harvested as previously described(8) *Candida albicans* UCH 60 was grown on Sabouraud Dextrose Agar, and suspended in sterile water. All cultures were standardised by direct viable cell count to contain approximately 108 viable cells/ml. 1ml of the test cultures was used to seed agar medium. 50µl of test solutions were for the antimicrobial tests.

The plates were incubated as previously described for bacteria(9) and those for the yeast at 37°C/48 hours.

Zones of inhibition due to the activity of the test solutions were measured. The diameters of the zones of inhibition were recorded as follows;

(i) - no activity at the concentration studies.

(ii) + diameter of inhibition zone up to 10mm.

(iii) + + diameter of inhibition zone 10-15mm.

(iv) + + + diameter of inhibition zone 15-20mm.

(v) + + + + diameter of inhibition zone above 20mm.

RESULTS AND DISCUSSIONS

The infrared spectra of the nitrato complexes (Table 2) are as commonly found in complexes where the nitrato group is covalently bonded through an oxygen atom. In such a case, the symmetry is lowered from a D_{3h} to a C_{2v} point group which is diagnostic of monodentate nitrato groups.

The spectra of the complexes show bands around 3300 cm^{-1} (Table 3) which have been assigned to the $^4A_2 \rightarrow {}^4T_1$ (F).

TABLE 3: ELECTRONIC SPECTRAL DATA.

Sample	Complex	*Band I $^4A_2 \rightarrow {}^4T_2(F)$	#Band II $^4A_2 \rightarrow {}^4T_1(F)$	Band III $^4A_2 \rightarrow {}^4T_1(P)$	
1	$[CoCl_2 I_2]^{2-}$	3333	5999	15528(1.17)+	17036(1.16), 19380(1.17), 44543(4.29)
2	$[CoCl_2Br_2]^{2-}$	3333	5999	15314(1.06)	19194(1.13), 47059(2.88)
3	$[CoBr_2I_2]^{2-}$	3400	6120	15529(1.10)	19194(1.10), 264500(3.17), 44643(4.09)
4	$[CoCl_2(ONO_2)_2]^{2-}$	3279	5902	15291(1.00)	17361(0.90), 19231(1.12), 43668(3.12)
5	$[CoI_2(ONO_2)_2]^{2-}$	3279	5902	15528(1.19)	26882(3.10), 45249(4.02)
6	$[CoBr_2(ONO_2)_2]^{2-}$	3247	5845	14925(0.99)	19380(1.04), 44843(3.51)
7	$[CoBrCl(ONO_2)_2]^{2-}$	3333	5999	15244(0.95)	19231(1.15), 4444(3.42)
8	$[CoClI(ONO_2)_2]^{2-}$	3279	5908	15337(0.97)	19193(1.17), 26882(3.25), 43384(3.47)
9	$[CoCl_2I_{(ONO2)}]^{2-}$	3257	5863	15700(1.20)	19231(2.00), 26954(3.11), 44643(4.09)
10	$[CoCl_2Br(ONO_2)]^{2-}$	3333	5999	15267(0.94)	19120(1.14), 44843(4.10)
11	$[CoBrI(ONO_2)_2]^{2-}$	3338	5999	15337(0.92)	19493(1.10), 25381(3.30), 44843(4.05)

*Observed in the near infrared region.
#Calculated from Jorgensen's relationship (14), Band II = 9/5 (Band I) cm^{-1}.
+ log ε values in parentheses.
All frequencies are in cm^{-1}.

TABLE 4: LIGAND FIELD PARAMETERS FOR THE TETRAHEDRAL COBALT (II) COMPLEXES.

Sample	Complex	#Band II (kK) $^4A_2 \rightarrow {}^4T_1(F)$	Band III (kK) $^4A_2 \rightarrow {}^4T_1(P)$	Dq (cm-1)	B (cm-1)	B/B_o =
1	$[CoCl_2I_2]^{2-}$	5.99	15.53 (1.17)*	343	747	0.77
2	$[CoCl_2Br_2]^{2-}$	5.99	15.31 (1.06)	353	736	0.76
3	$[CoBr_2I_2]^{2-}$	6.12	15.53 (1.10)	370	739	0.77
4	$[CoCl_2(ONO_2)_2]^{2-}$	5.90	15.29 (1.00)	294	734	0.76
5	$[CoI_2(ONO_2)_2]^{2-}$	5.90	15.52 (1.19)	348	739	0.76
6	$[CoBr_2(ONO_2)_2]^{2-}$	5.84	14.93 (0.99)	344	718	0.74
7	$[CoBrCl(ONO_2)_2]^{2-}$	5.99	15.24 (0.95)	348	726	0.75
8	$[CoClI(ONO_2)_2]^{2-}$	5.90	15.34 (0.97)	294	734	0.76
9	$[CoCl_2I(ONO_2)]^{2-}$	5.86	15.70	348	773	0.79
10	$[CoCl_2Br(ONO_2)]^{2-}$	5.99	15.23 (0.94)	352	734	0.76
11	$[CoBrI(ONO_2)_2]^{2-}$	5.99	15.34	362	756	0.78

B_o = 967 cm^{-1} = Racah parameter for the free metal ion (8).
B = Racah parameter for the metal ion in the complex.
*log ε values in parentheses.
1kK = 1000 cm^{-1}

TABLE 5: RESULTS SHOWING ANTIMICROBIAL ACTIVITY OF THE COABLT COMPLEXES.

Sample solution	E. coli	Ps. Aeruginosa	B. cereus	Staph. Aaureus	Candida albicans
1	+ +	+ +	+ +	+ +	+ +
2	+ + +	+ +	+ +	+ + + +	+ +
3	+ +	+ +	+ + +	+ +	+ +
4	+ + +	+ +	+ + +	+ +	+ +
5	+ + + +	+ +	+ + +	+ + + +	+ +
6	+ + + +	+ + +	+ + +	+ + + +	+ + + +
7	+ + + +	+ + +	+ + +	+ + + +	+ + + +
8	+ + +	+ +	+ + +	+ + + +	+ + + +
9	+ + + +	+ +	+ + +	+ + + +	+ + + +
10	+ + +	+ +	+ +	+ + + +	+ +
11	+ +	+ +	+ +	+ +	+ +
Cobalt (II) Chloride	+ +	+ +	+ +	+ +	+ +
TAC	-	-	-	-	-
QAC (+ ve control)	+ + + +	+ + +	+ + + +	+ + + +	+ + + +

The second transitions were calculated and were found in the 6000cm^{-1} neighbourhood.

All the complexes gave broad bands in the 1400-19000 cm^{-1} region. The iodo-complexes in particular show a band in the 25000 -30000 cm^{-1} (log ε, 3 - 3.5) region, which is likely to be of charge-transfer origin. A very broad and symmetric band in the range 44000 - 46000 (log ε, 3.5 - 4.1) found in the spectra of the complexes are due to intra-ligand transitions.

The values of the crystal field parameters indicated in Table 4 were determined using "Transition Energy Ratios"(10). The Dq values obtained from these calculations range from 294 to 370 cm^{-1} while the Racah parameter B, falls in the 718 - 773 cm^{-1} range compared with B = 967 cm^{-1} for the free metal ion.

Previously reported tetrahalocobaltate(II) ions have characteristic greenish to bluish colours diagnostic of tetrahedral geometry(1,11). The colour of the complexes(1-11) reported in this work range from green to dark blue(Table 1).

Massabni and Serra(12) attributed $CoL_2(NO_3)_2$ complexes having violet to pinkish colours to octahedral geometry where the nitrate groups behave as bidentate species with $\beta > 0.80$ values.

Consequently, Cobaltate (II) complexes having greenish to blue colour and a β value less than 0.80 should be considered diagnostic for cobalt (II) in a tetrahedral environment.

Table 5 shows the antimicrobial activity of the Cobalt (II) complexes. The results show that Cobalt (II) complexes are showing activity either comparable with or greater than that of the simple cobalt (II) chloride. In aqueous solutions, both complex and Co(II) chloride yield $[Co(H_2O)_6]^{2+}$ cation, and in addition, the TAC also produces $(C_2H_5)_4N^+$ ions which probably enhances the activity of these complexes more than a simple Co(II) chloride.

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