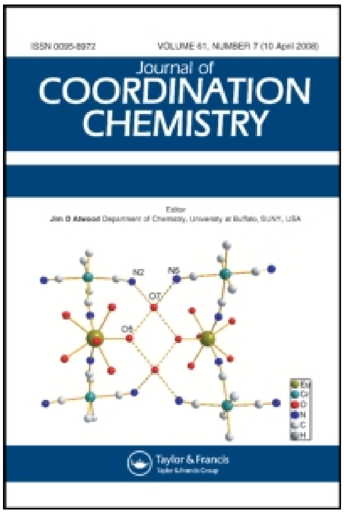

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TETRAHEDRAL COBALT(II) COMPLEXES OF 2, 3-DIPHENYL-2, 3-DEHYDROTETRAZOLIUM-5-THIOLATE (DEHYDRODITHIZONE)

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The following solid cobalt(II) complexes of 2, 3-diphenyl-2, 3-dehydrotetrazolium-5-thiolate (dehydrodithizone) (L) were prepared: CoL_2X_2 (X = Cl($4H_2O$), Br(H_2O)), CoL_3X_2 (X = Br(½H_2O), I), $CoL_4X_2 \cdot 2H_2O$(X = Br, I, ClO_4, BF_4). All the complexes are green and have magnetic moments corresponding to a cobalt(II) tetrahedral coordination. The ligand is monodentate and sulphur-bonded to the metal. The far infrared and electronic spectra of the solids show that three types of chromophores are present: $[CoL_2X_2]$ in $[CoL_2Cl_2] \cdot 4H_2O$, $[CoL_2Br_2]L_2 \cdot 2H_2O$ and $[CoL_2Br_2] \cdot H_2O$, $[CoL_3X]$ in $[CoL_3Br]Br \cdot ½H_2O$ and $[CoL_3I]I$ and $[CoL_4]$ in $[CoL_4]X_2 \cdot 2H_2O$ (X = I, ClO_4, BF_4). The tendency to form "mixed" chromophores decreases in the order Cl > Br > I. The electronic structural parameters were calculated; β values decrease in the order $[CoL_2Cl_2] > [CoL_2Br_2] > [CoL_3Br]^+ > [CoL_4]^{++}$ in agreement with the nephelauxetic order Cl > Br > S.

INTRODUCTION

The oxidation product of dithizone known[1–3] as "dehydrodithizone" ($C_{13}H_{10}N_4S$) has been denominated "anhydro-5-mercapto-2, 3-diphenyltetrazolium hydroxide" by Kushi *et al.*[4–5], who determined its crystal structure, and "2, 3-diphenyl-2, 3-dehydrotetrazolium-5-thiolate" (DDTT) by Bigotto *et al.*,[6] who studied its infrared spectrum. An isomer of this compound may be obtained from glacial acetic acid; its crystal structure has been determined by McDonald *et al.*[7] DDTT has metal complexing properties, but so far only the solid dimer complex $[(DDTT)HgCl_2]_2$ has been isolated: its crystal structure[8,9] shows that it acts as monodentate ligand sulphur bonded to the metal. A square planar complex (DDTT) $AuCl_3$ has been identified in solution[10] and for this complex too a metal-sulphur coordination has been assumed. Since few data are available in the literature regarding the DDTT-complexes we are systematically studying the coordination compounds of this ligand with several metals. The cobalt(II) complexes are described and discussed in the present work.

EXPERIMENTAL

The ligand was prepared by oxidation of dithizone with potassium hexacyanoferrate(III)[3] and recrystallized from ethanol. All the reagents were of the best chemical grade. Acid used: HCl 37%, HBr 48%, HI 57%, $HClO_4$ 60%, HBF_4 31%.

The complexes were prepared by adding a warm solution of $CoCO_3$ in a minimum volume of a 10% aqueous solution of the corresponding acid to a warm solution of the ligand in ethanol 95%; the compounds precipitate in a microcrystalline state. $CoL_2Cl_2 \cdot 4H_2O$: 1 mM Co in 2 ml HCl to 2 mM L in 30 ml EtOH and cooling the solution very rapidly; $CoL_4Br_2 \cdot 2H_2O$: 1 mM Co in 2 ml HBr to 4 mM L in 100 ml EtOH and cooling the solution very rapidly; $CoL_3Br_2 \cdot ½H_2O$: 1 mM Co in 2 ml HBr + 5 ml EtOH to 2 mM L in 30 ml EtOH and cooling very slowly; $CoL_2Br_2 \cdot H_2O$: 1 mM Co in 2 ml HBr + 5 ml EtOH to 1 mM L in 30 ml EtOH and cooling; $CoL_4I_2 \cdot 2H_2O$: 1 mM Co in 2 ml HI to 2 mM L in 80 ml EtOH and cooling; CoL_3I_2: 1 mM Co in 2 ml HI + 5 ml EtOH to 1 mM L in 30 ml EtOH and cooling; $CoL_4(ClO_4)_2 \cdot 2H_2O$: 1 mM Co in 6 ml $HClO_4$ to 2 mM L in 80 ml EtOH; $CoL_4(BF_4)_2 \cdot 2H_2O$: 1 mM Co in 6 ml HBF_4 to 2 mM L in 80 ml EtOH.

The compounds were analysed by standard methods (Table 1). Molar conductivities were measured with a WTW conductivity bridge at 25°C. Magnetic susceptivities were determined by the Gouy method. Their correction with the Pascal

TABLE 1.

Analytical data, found % (calcd. %). Molar conductivities Λ_M(Ω^{-1}, mol^{-1}, cm^2) on 10^{-3} M solutions in nitromethane (NMT) and dimethylformamide (DMF). Colour in mass of the complexes.

	M	C	N	H	Λ_M		Colour
					NMT	DMF	
$CoL_2Cl_2 \cdot 4H_2O$	7.88(8.29)	44.20(43.95)	16.01(15.77)	3.60(3.97)	6	50	deep green
$CoL_4Br_2 \cdot 2H_2O$	4.70(4.63)	48.70(49.05)	16.96(17.62)	3.75(3.49)	25	91	brown green
$CoL_3Br_2 \cdot ½H_2O$		47.46(47.28)	17.14(16.97)	3.33(3.15)	20	110	green
$CoL_2Br_2 \cdot H_2O$		41.68(41.89)	15.30(15.03)	3.09(2.98)	30	98	green
$CoL_4I_2 \cdot 2H_2O$	4.40(4.31)	46.22(45.72)	16.49(16.40)	3.29(3.25)	57	140	bright green
CoL_3I_2		43.83(43.54)	15.75(15.62)	3.15(2.81)	37	118	green
$CoL_4(ClO_4)_2 \cdot 2H_2O$	4.34(4.49)	47.15(47.63)	17.02(17.09)	3.21(3.38)	143	133	green
$CoL_4(BF_4)_2 \cdot 2H_2O$	4.50(4.58)	48.96(48.57)	17.15(17.43)	3.40(3.45)	119	138	green

TABLE 2.

Far infrared spectra (cm^{-1}) of the solids in nujol mulls on polythene.

	DDTT	$CoL_2Cl_2 \cdot 4H_2O$	$CoL_4Br_2 \cdot 2H_2O$	$CoL_4I_2 \cdot 2H_2O$	$CoL_4(ClO_4)_2 \cdot 2H_2O$	$CoL_4(BF_4)_2 \cdot 2H_2O$
Ligand bands	392m	391w	391w	392w	391w	391w
	360sh	360sh		352sh	375w	378w
	351ms	354vw	353w	340mb	343ms	343mb
	305m	306sh	304w	302mw	303wm	304m
	281w	280sh	280w	273m	274mb	275mb
	220ms	224mw	[226s, sh]	223wm	220sh	218w
	149w	147sh	148mw	147w	148w	147w
	131sb	[127smb]	125vw	126w	127w	128w
	90ms	86mw	87mw	85mw	86mw	86mw
ν(MS)		315w	316w	316m	318ms	318m
				245w	249sh	247w
ν(MX)		301vs	237vs			
		292sh	226s, sh			
δ(MX)		127smb	98mw			
Other bands		209sh	209sh	200wb	200mb	196wb
				118w	120mw	119mw

TABLE 4

Averaged $\bar{\nu}_3$ and $\bar{\nu}_2$ (kK) bands, derived electronic structure parameters Dq(cm^{-1}), B(cm^{-1}); β; T.I.P. = 2.09/10Dq[16]; magnetic moments (B.M.) (A) corrected for Pascal constants only, (B) corrected for Pascal constants and T.I.P.

Compound	$\bar{\nu}_3$	$\bar{\nu}_2$	Dq	B	β	T.I.P.	B.M.(A)	B.M.(B)
$CoL_2Cl_2 \cdot 4H_2O$	14.75	5.56	319	716	0.737	656	4.46	4.37
$CoL_4Br_2 \cdot 2H_2O$	14.30	5.13	293	708	0.729	714	4.67	4.50
$CoL_2Br_2 \cdot H_2O$	14.45	5.61	322	691	0.712	488	4.40	4.28
$CoL_3Br_2 \cdot ½H_2O$	14.75	6.76	392	650	0.670	592	4.59	4.42
$CoL_4I_2 \cdot 2H_2O$	14.65	7.35	433	600	0.618	483	4.75	4.65
$CoL_4(ClO_4)_2 \cdot 2H_2O$	14.60	6.67	408	602	0.620	512	4.66	4.53
$CoL_4(BF_4)_2 \cdot 2H_2O$	14.60	6.67	408	602	0.620	512	4.55	4.45

TABLE 3.
Electronic spectra (kK) of the solid complexes in nujol mulls on filter paper.

	ν_2					ν_3					Other bands			
$CoL_2Cl_2 \cdot 4H_2O$	4.60sh	4.87sh	5.12sh	5.47sh	5.99s	14.23vs	14.80vs	15.40sh	15.60s	16.03sh	18.68vw			
$CoL_4Br_2 \cdot 2H_2O$		4.61sh		5.02sh	5.60s	13.66s	14.12s	14.80s	15.26s	16.38sh	19.16vw			
$CoL_3Br_2 \cdot ½H_2O$	4.65w	6.13s	6.90w	7.54w	8.55s	13.33sh		14.75vs	15.38sh	16.13sh		24.39sh	25.51sh	26.88vs
$CoL_2Br_2 \cdot H_2O$	4.65sh	5.75vs	6.90sh	7.46sh		13.16sh	13.64s	14.28s	14.84s	15.46s	16.67sh			
$CoL_4I_2 \cdot 2H_2O$	4.93vw	6.10sh	6.97vw	7.58vw	8.69sb			14.60vvs	15.32sh	16.02sh	18.20sh	23.25sh	25.25vs	26.30vs
CoL_3I_2*						13.51sh	14.66vs	15.29sh		16.92sh			25.25vs	27.74vs
$CoL_4(ClO_4)_2 \cdot 2H_2O$	4.70w	5.88sh	6.67m	7.55s	8.51sh			14.50vvs	15.35w	16.13sh	18.20sh	23.52sh	25.13sh	26.46vs
$CoL_4(BF_4)_2 \cdot 2H_2O$	4.71w	5.88sh	6.67m	7.61s	8.42sh			14.50vvs	15.28w	16.18w		23.55sh	25.13s	26.46vs
Ligand											14.92sh	21.65vs	24.75vs	

(*) not recorded above 800 nm.

constants or with the experimental magnetic molar susceptivity of the ligand ($\chi_M = -119.5 \cdot 10^{-6}$) gave approximately the same results. Infrared spectra (Table 2) were recorded on the solids in KBr disks (4000–250 cm^{-1}) with a Perkin–Elmer 521 spectrophotometer and in nujol mulls on polythene (400–60 cm^{-1}) with a Hitachi FIS3 spectrophotometer. The electronic spectra (Table 3) were recorded on the solids in nujol mulls on filter paper with a Shimadzu MPS-50L spectrophotometer and on the solutions with a Beckman DK1A spectrophotometer.

RESULTS AND DISCUSSION

Cobalt(II) complexes of DDTT (Table 1) show several stoichiometries: CoL_2A_2 (A = Cl, Br), CoL_3A_2 (A = Br, I) and CoL_4A_2 (A = Br, I, ClO_4, BF_4) depending on the anion and on the preparation conditions; all the complexes have a more or less deep green colour. Their magnetic moments (Table 4) lie in the range expected (4.3–4.8 B.M.) for tetrahedral cobalt(II) complexes.[10]

The molar conductivities (Table 1) are not very significant because the complexes undergo some transformation in nitromethane and in dimethylformamide solutions, as is shown by their electronic spectra which are very different from those of the solids. However the conductivities indicate that the perchlorate and fluoborate have an almost normal behaviour of 1:2 electrolytes in both solvents, the complex $CoL_4I_2 \cdot 2H_2O$ has the same behaviour in the more polar dimethylformamide while in nitromethane stronger interactions occur between the iodide ion and the cationic complex. Similar interactions may occur for the other complexes in both solvents.

The *infrared spectra* of the complexes from 4000 and 400 cm^{-1} do not give any important information on the metal-ligand bonding because the ν(CN) and ν(CS) modes are not independent but mixed or coupled with the vibration modes of the rigid tetrazole ring. The medium-strong band of the ligand at 828 cm^{-1}, to which a 21% of ν(CS) contribution was assigned,[6] becomes very weak in the complexes and two new weak bands appear at 705–730 cm^{-1}. These may be due to a splitting of some ligand bands in the complexes or indicate a decrease in the ν(CS) frequency in consequence of a sulphur coordination of the ligand to the metal, which seems to be the normal type of metal-ligand bonding for DDTT[8–10]

The *far infrared* (400–60 cm^{-1}) bands of the ligand (Table 2) may be clearly identified in the spectra of the complexes without any important positional shift. The halides $CoL_2Cl_2 \cdot 4H_2O$ and $CoL_4Br_2 \cdot 2H_2O$ very distinctly show three new mass-sensitive bands of which two may be assigned to ν(CoX) modes and one, presumably to a δ(CoX) mode. The ν(CoX) frequencies agree well with other values in the literature for ν(CoX) terminal modes in a tetrahedral coordination.[12–14] The ν(CoBr)/ν(CoCl) ratios, 237/301 = 0.78, 226/292 = 0.77 and 98/127 = 0.77, are in the range of values expected for complexes having similar structures.[15] The complex $CoL_2Br_2 \cdot H_2O$ also shows two very strong bands at 233 and 225 cm^{-1}, and the complex $CoL_3Br_2 \cdot \frac{1}{2}H_2O$ only a medium band at 227 cm^{-1}. The iodides do not show bands assignable to ν(CoX) modes.

A ν(CoS) band may be identified for all the complexes at 315–320 cm^{-1} and a second ν(CoS) band at 245–250 cm^{-1} for the complexes CoL_4A_2 (A = I, ClO_4, BF_4), in agreement with ν(CoS) values found in the literature for Co(II) tetrahedral complexes.[13]

The perchlorato and fluoborato anions are not coordinated: their ν_3 bands (1089 and 1048 cm^{-1}, respectively) show only weak shoulders and their ν_4 bands (619 and 516 cm^{-1}, respectively) are not split, the ν_1 (926 cm^{-1}) and ν_2(425 cm^{-1}) bands of the perchlorate are weak while those of the fluoborate are masked by other bands of the complex. A slight deviation of these ions from the T_d symmetry, if present, may depend on localized interactions in the crystal lattice.

The *electronic spectra* of the solids (Table 3) show two strong multiple bands in the regions where the ν_2 and ν_3 bands of the cobalt(II) tetrahedral complexes normally appear. The positions and the shapes of these bands clearly correspond to two types of complexes. For the complexes $CoL_2Cl_2 \cdot 4H_2O$, $CoL_4Br_2 \cdot 2H_2O$ and $CoL_2Br_2 \cdot H_2O$ the ν_3 band shows three or four peaks of almost equal intensities between 640 and 730 nm and the ν_2 band extends between about 1500 and 2300 nm. For the complexes $CoL_3Br_2 \cdot \frac{1}{2}H_2O$, $CoL_4I_2 \cdot 2H_2O$, CoL_3I_2, $CoL_4A_2 \cdot 2H_2O$ (A = ClO_4, BF_4) the ν_3 band shows a very intense peak at about 680 nm with shoulders, and the ν_2 band extends between 1000 and 1800 nm; for these complexes a very strong band is observed at about 375 nm with a strong shoulder at about 395 nm, in the region, that is, where the ligand also shows two very strong bands.

As in other tetrahedral cobalt(II) complexes,[16] more peaks are present than the three normally due to splitting by spin-orbit coupling; the number and energy spread of these bands was attributed to dynamic Jahn–Teller effects in the excited states.[16] The selection of the true values of the ν_2 and ν_3 bands is therefore rather difficult, particularly in the case of the spectra of solid compounds. This selection was performed in this case by taking the centre of gravity of the total intensity, as suggested by Cotton *et al.*[16]

From these averaged $\bar{\nu}_2$ and $\bar{\nu}_3$ energies (Table 4) the values of Dq and B were calculated by using the method of Underhill and Billing;[17] the β values were calculated by assuming a value of B for the free ion of 971 cm^{-1}.[18] By using the relation given by Cotton *et al*,[16] the values of T.I.P. = 2.09/10 Dq were calculated (Table 4). The magnetic moments obtained by correcting the magnetic susceptivities only for the Pascal constants and also for the temperature independent paramagnetism are reported in Table 4. Both series of values well agree with a tetrahedral coordination.

The $\bar{\nu}_3$, $\bar{\nu}_2$, Dq, B and β values of the complexes $CoL_2Cl_2 \cdot 4H_2O$ and $CoL_4Br_2 \cdot 2H_2O$ are very close to those found[16] for the corresponding tetrahalo-anions. This could mean that the electronic spectra of these complexes arise from the $[CoX_4]^=$ anion of a $[CoL_4][CoX_4]$ complex with 4 ligand molecules not coordinated for the bromide. However, the characteristic bands of the $[CoL_4]^{++}$ cation, as discussed below, are not observed either in the electronic or in the infrared spectra of these complexes. Therefore, the structure $[CoL_2X_2]$ must be assigned to these tetrahedral chromophores, and for the compound $CoL_4Br_2 \cdot 2H_2O$ two molecules of the ligand must be considered as not being bonded to the metal. This conclusion may be supported by the fact that the infrared and electronic spectra and the spectral parameters of the complex $[CoL_2Br_2] \cdot H_2O$ are very similar to those of the $[CoL_2Br]L_2 \cdot 2H_2O$ complex.

The almost identical electronic and far infrared spectra of the complexes $CoL_4A_2 \cdot 2H_2O$ (A = I, ClO_4, BF_4) clearly indicate that the chromophore is the tetrahedral cation $[CoL_4]^{++}$; the infrared spectra show that the anion is not coordinated. The electronic structural parameters Dq, B and β of these three complexes are also similar or equal, within experimental error.

The Dq, B and β parameters of the $[CoL_2Cl_2] \cdot 4H_2O$ and $[CoL_2Br_2]L_2 \cdot 2H_2O$ complexes are very much closer to those of the corresponding tetrahalo-anions $[CoX_4]^=$ than to those of the $[CoL_4]^{++}$ cation, even if they are "mixed" complexes for which the "average ligand field approximation"[16] should give values for these parameters somewhere between those of the $[CoX_4]^=$ and $[CoL_4]^{++}$ chromophores. This may indicate that in these "mixed" chromophores the spectroscopic effect of the halide ion is stronger than that of the sulphur ligand.

The complex $CoL_3Br_2 \cdot ½H_2O$ shows a medium broad band at 227 cm^{-1} which may correspond to the ligand band at 220 cm^{-1} or to the superimposition of this band onto the single ν(CoBr) band expected for a monobromo-coordinated $[CoL_3Br]Br$ complex. This band should be weaker than in the other two complexes $[CoL_2Br_2]L_2 \cdot 2H_2O$ and $[CoL_2Br_2] \cdot H_2O$, in which two almost superimposed ν(CoBr) bands at about 235 and 225 cm^{-1} reinforce each other. This "mixed" $[CoL_3Br]$ coordination seems to be supported also by the spectral parameters of this complex, which are "intermediate" between those of the $[CoL_2X_2]$ and the $[CoL_4]^{++}$ complexes. This is particularly true for the β values, which decrease in the order $[CoL_2Cl_2] > [CoL_2Br_2] > [CoL_3Br]^+ > [CoL_4]^{++}$, in good agreement with the nephelauxetic order $Cl > Br > S$.[18] A similar structure could be proposed for the complex CoL_3I_2, even if sufficient experimental data could not be collected. The fact that this complex is obtained from solutions containing a large excess of hydrogen iodide and of cobalt ion (cobalt:ligand ratio = 1:1) indicates that iodide ion cannot form the complex $[CoL_2I_2]$ as the other two halides do. All the data discussed above show that the tendency to form the "mixed" complexes decreases in the order $Cl > Br > I$.

The fact that complexes of different stoichiometry and structure may be obtained from solutions with very similar composition is not easy to explain. In the case of the iodides, the formation of CoL_3I_2 may be due to the presence of an excess of iodide and cobalt ions greater than that used for the preparation of the complex $CoL_4I_2 \cdot 2H_2O$, but for the bromide this condition does not seem to be sufficient. It seems that a very rapid precipitation of the complex favours the formation of the $[CoL_2Br_2]$ complex even in the presence of a large excess of the ligand, as in the case of the $[CoL_2Br_2]L_2 \cdot 2H_2O$ compound. The formation of these complexes may follow a reaction mechanism of the type

$$\begin{aligned}[CoX_4]^= &\xrightarrow{+2L-2X^-} [CoX_2L_2]\\ &\xrightarrow{+2L-2X^-} [CoL_4]^{++}.\end{aligned}$$

It was not possible to investigate this mechanism because of the rather low solubility of the complexes at room temperature, and because even the mother solutions of the complexes have electronic spectra that are quite different from those of the solid compounds.

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