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Substituent Effect on the Spectrochemical Properties of Cobalt(II) Halide Complexes with N-Monosubstituted 1,3-Imidazolidines-2-thione

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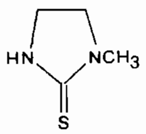
By reacting cobalt(II) halides with N-methyl and N-ethyl-1,3-imidazolidine-2-thione, CoL_2X_2 complexes (X = Cl, Br, I) are obtained. The infrared spectra show them to be S-bonded to the metal; the νCoS vibrations are located within 340–320 cm^{-1}. Colours, magnetism and electronic spectra support a tetrahedral stereochemistry. Using the average ligand field approximation, Dq and B′ values for $[CoL_4]^{2+}$ are evaluated and the ligands are inserted in the spectrochemical and nephelauxetic series. The Dq values seem to depend on the electron releasing effect of the alkyl groups.

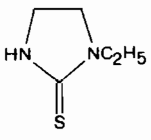
Introduction

The substituent effect on Dq parameter for S-bonded complexes of cobalt(II) with five-membered thiolactams in tetrahedral environments has been studied by Madan and Sulich [1]. Unlike what was found for octahedral Ni(II) complexes [2], where significant variations of Dq were observed and interpreted on the basis of steric effect, the cobalt(II) complex with N-methyl-pyrrolidine-2-thione showed the Dq parameter (338 cm^{-1}) larger than that of the unsubstituted derivative (326 cm^{-1}). This was explained on the basis of the inductive effect of the methyl, since in the tetrahedral configuration there is not steric repulsion among the ligands.

Pursuant to our interest in the coordination chemistry with five-membered rings containing the thioamido group, we prepared the complexes of N-methyl- and N-ethyl-1,3-imidazolidine-2-thione with Co(II) halides in order to compare their spectrochemical parameters with those reported by Carlin and Holt [3] for 1,3-imidazolidine-2-thione.



(ditme)



(ditet)

Results and Discussion

The analytical data and some physical properties of the cobalt complexes with ditme and ditet are reported in Table I. The colours of the complexes suggest a probable tetrahedral stereochemistry. The conductivity data show that all the compounds are non-electrolytes, although the iodo-derivatives have some degree of solvolysis. This is in accord with the $[CoL_2X_2]$ formulation, as found for ethylenethiourea [3] and pyrrolidine-2-thione [1].

TABLE I. Analytical Data and Some Physical Properties.

Compound	Colour	Found (calcd.)%			M.p. (°C) dec.	Λ_M^{a}
		C	H	N		
$Co(ditme)_2Cl_2$	clear blue	26.0 (26.5)	4.3 (4.45)	15.0 (15.5)	160	2.2
$Co(ditme)_2Br_2$	dark blue	21.2 (21.3)	3.5 (3.6)	12.5 (12.4)	190	4.2
$Co(ditme)_2I_2$	green	17.7 (17.6)	2.8 (3.0)	10.3 (10.3)	170	7.0
$Co(ditet)_2Cl_2$	clear blue	30.7 (30.8)	5.3 (5.2)	14.4 (14.4)	160	2.4
$Co(ditet)_2Br_2$	dark blue	25.2 (25.1)	4.2 (4.2)	11.7 (11.7)	130	4.0
$Co(ditet)_2I_2$	pea-green	21.0 (21.0)	3.4 (3.5)	9.9 (9.8)	110	10.9

$^a\Omega^{-1}$ cm^2 mol^{-1} in acetone at 15 °C.

Infrared Spectra

Although these ligands have more reaction sites able to coordinate the metals, they usually behave as monodentate through the sulphur atom [4–5]. The infrared spectra of the complexes (see Table II) show that the coordination link occurs through sulphur

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TABLE II. Principal Bands (4000–200 cm^{-1}) of the Free Ligands and Their Co(II) Complexes (Solid Phase).

Compound	νNH	νCN + δNH	νCS	νCoS	νCoX	Other vibrations down to 400 cm^{-1}
ditme[a]	3200vs	1525vs	518vs	–	–	398m–286s
Co(ditme)$_2$Cl$_2$	3270vs	1540vs	500s	330sh–321sbr	321sbr–293ms	400w
Co(ditme)$_2$Br$_2$	3290vs	1540vs	502s	328sbr	254sh–237vs	400w–387w–288ms
Co(ditme)$_2$I$_2$	3300vs	1540vs	500s	328sbr	<210	400w–387w–288ms–252w
ditet[a]	3200vs	1505vs	513s	–	–	367m–287s
Co(ditet)$_2$Cl$_2$	3310vs	1525vs	502s	337sh–320sbr	320sbr–302shbr	245wbr
Co(ditet)$_2$Br$_2$	3310vs	1525vs	500s	333sh–322sbr	252ms–227w	374m
Co(ditet)$_2$I$_2$	3350vs	1525vs	500s	336m–323m	215s	374mw

[a]Assignments according to ref. 6.

TABLE III. Magnetic Susceptibility Measurements

Compound	Dia.corr.[a] ×10^6	T.I.P.[b] ×10^6	T °K	χ_M^{corr} [c] ×10^6	ρ[d]	μ_{eff}[e]	θ °K
Co(ditme)$_2$Cl$_2$	–191	602	146	18910	0.993	4.87	–6.5
			175.5	16510			
			204.5	14140			
			226	12410			
			260	11060			
Co(ditme)$_2$Br$_2$	–212	631	147.5	21220	1.000	4.91	6.5
			175	17760			
			203	15230			
			231.5	13220			
			260	11830			
Co(ditme)$_2$I$_2$	–240	640	153.5	23450	1.000	5.04	19.4
			179	19690			
			206	16850			
			232.5	14860			
			261	12980			
Co(ditet)$_2$Cl$_2$	–206	608	125	24440	0.999	4.58	18.5
			178	16310			
			204.5	13920			
			232.5	12280			
			260	10730			
Co(ditet)$_2$Br$_2$	–230	611	125	24480	1.000	4.50	23
			153	19280			
			205	13580			
			232.5	11970			
			260	10530			
Co(ditet)$_2$I$_2$	–258	615	125	24100	1.000	4.53	18.9
			175	16260			
			200	14085			
			234	11835			
			260	10580			

[a]Calculated from Pascal's constants. [b]Temperature independent paramagnetism was calculated from the expression T.I.P. = 2.09/10 Dq (Dq in cm^{-1}). [c]χ_M^{corr} is the molar susceptibility corrected for diamagnetism and T.I.P. [d]Correlation coefficient of the straight lines 1/χ_M^{corr} *versus* T. [e]Calculated from the equation $\mu_{eff} = 2.84[\chi_M^{corr}\cdot(T - \theta)]^{1/2}$.

also in this case. In fact, the very strong bands at *ca.* 1500 cm^{-1}, reported as νCN + δNH [6], undergo upward shifts of *ca.* 17 cm^{-1} in the complexes, indicating an increase of the π-bond order on CN link. To this increase, a decrease of the π-bond order on CS would be expected as found in the lowering of the two bands at 518 and 513 cm^{-1}, due to the prevailing νCS vibration in ditme and ditet respectively [6]. The

νCN and νCS behaviour is enough to attribute the S-coordination to the cobalt, since analogous trend is verified for the same bands in the S-methiodide derivatives of ditme and ditet [6]. On the other hand, the NH nitrogen cannot be responsible of the coordination, since the νNH moves in the complexes towards higher wavenumbers. Hence, assuming a tetrahedral environment as will be clear from the spectral measurements reported in a subsequent section, the complexes have C_{2v} local symmetry. Then two cobalt–halogen ($A_1 + B_1$) and two cobalt–sulphur ($A_1 + B_2$) vibrations are expected in the infrared spectrum. Literature reports the νCoS vibrations falling down to 300 cm^{-1} [7, 8]; here, no bands common to the two series of complexes are present below 300 cm^{-1}, while there are strong broad absorptions at *ca.* 325 cm^{-1}, which can arise from the two νCoS vibrations. νCoX's are reported in the last but one column of Table II and the assignments agree well with the literature [7–9].

Magnetism

The magnetic susceptibilities are reported in Table III. The measurements were carried out at different temperatures within 125–260 °K and the molar susceptibility values were corrected both for diamag-

TABLE IV. Electronic Spectra of Cobalt(II) Tetrahedral Complexes

Complex	Solvent	$^4T_1(F) \leftarrow {}^4A_2$ ν_2 (cm^{-1})	$^4T_1(P) \leftarrow {}^4A_2$ ν_3 (cm^{-1})	
			a	b
$Co(ditme)_2Cl_2$	Acetone	–	15823(363)	16393(489)
			15060(353)	15060(526)
			14245(300)	13774(403)
	Solid	7143	16000	
		5115	14771	
			13793	
$Co(ditme)_2Br_2$	Acetone	–	15480(466)	15723(536)
			14620(491)	14598(626)
			13889(416)	13699(632)
	Solid	7143	15456	
		5480	14184	
			13158	
$Co(ditme)_2I_2$	Acetone	–	14837(568)	14925(571)
			14006(653)	13889(791)
			13263(568)	13055(815)
	Solid	6897	15456	
		5405sh	13514	
			12500	
$Co(ditet)_2Cl_2$	Acetone	–	16290(381)	16393(458)
			15152(401)	15152(500)
			14164(330)	13889(346)
	Solid	8000sh	15924	
		6896	14815	
		5362	13793	
$Co(ditet)_2Br_2$	Acetone	–	15576(472)	15723(540)
			14620(507)	14663(551)
			13889(441)	13736(520)
	Solid	6944	15823	
		5128	14749	
			13333	
$Co(ditet)_2I_2$	Acetone	–	14750(571)	15015(600)
			13928(631)	13966(711)
			13193(523)	13089(715)
	Solid	6536	14286	
		5000	13928	
			12739	

The molar extinction coefficients (l cm^{-1} mol^{-1}) are reported in parentheses.

[a] From 1×10^{-3}–3×10^{-3} solutions of the complexes in acetone at 15 °C.

[b] From (a) with a large excess of ligands ([ditme] = 0.1727 *M*; [ditet] = 0.1694 *M*).

netism and T.I.P. (temperature independent paramagnetism). μ and θ were obtained from the straight lines of $1/\chi_M^{corr}$ *versus* T. The obtained values of μ_{eff} fall in the expected range for tetrahedral cobalt(II) [10].

Electronic Spectra

The electronic spectra of the complexes are reported in Table IV. The spectra in acetone solution were recorded without and in presence of an excess of ligands. The increase of the molar extinction coefficient indicates the presence of solvolysis equilibria in solution. The ϵ values are coherent with a tetrahedral structure and they increase on passing from chlorine to iodine. Although the complexes have C_{2v} local symmetry, nevertheless the surrounding of Co(II) is considered as belonging to the T_d point group; hence, the bands are reported as ν_2 ($^4T_1(F) \leftarrow {}^4A_2$) and ν_3($^4T_1(P) \leftarrow {}^4A_2$). In order to evaluate the spectrochemical parameters by means of the equations of Tanabe and Sugano [11] the ν_2 and ν_3 were chosen according to Cotton *et al.* [12] by visual estimation. In Table V ν_2 and ν_3 together with the spectrochemical parameters are reported.

TABLE V. Electronic Spectra and Parameters for the Tetrahedral Cobalt(II) Complexes.

Compound	ν_3[a] cm^{-1}	ν_2[a] cm^{-1}	Dq cm^{-1}	B′ cm^{-1}	β[b]
$Co(ditme)_2Cl_2$	15040	6024	347	710	0.73
$Co(ditme)_2Br_2$	14510	5760	331	689	0.71
$Co(ditme)_2I_2$	13700	5650	326	638	0.66
$Co(ditet)_2Cl_2$	14925	5970	344	705	0.73
$Co(ditet)_2Br_2$	14600	5935	342	685	0.71
$Co(ditet)_2I_2$	13640	5880	340	621	0.64

[a] Evaluated according to ref. 12. [b] B (free ion) 967 cm^{-1} according to ref. 16.

TABLE VI. Dq, B′ and β Values Calculated Using the Average Ligand Field Approximation.

	$Co(etu)_4^{2+}$	$Co(ditme)_4^{2+}$	$Co(ditet)_4^{2+}$
Dq	374(378)[a]	382	397
B′	634(651)[a]	668	651
β	0.66(0.67)[a]	0.69	0.67

[a] From $Co(etu)_4(ClO_4)_2$; ref. 1.

By comparing these values with those obtained by Carlin and Holt [3] for the ethylenethiourea derivatives (Dq = 339, 332, 321 cm^{-1}; B′ = 693, 665, 629 cm^{-1} for Cl, Br and I complexes respectively) one can observe that they are very close. However, in order to insert these ligands in the spectrochemical and nephelauxetic series, we used the average ligand field approximation to estimate the electronic parameters of $[CoL_4]^{2+}$ (L = ditme and ditet). The results are reported in Table VI, together with the corresponding values obtained from $Co(etu)_2X_2$ (X = Cl, Br, I; etu = ethylenethiourea) [3]. Near these values, Dq, B′ and β obtained from $[Co(etu)_4](ClO_4)_2$ [3] are in parentheses. Dq's, thus obtained, allow us to locate these molecules in the following spectrochemical series for tetrahedral Co(II) complexes with ligands containing the thioamido group: pyrrolidine-2-thione (326) [1] < N-methyl-pyrrolidine-2-thione (338) [1] < ethylenethiourea (378) [3] < N-methyl-1,3-imidazolidine-2-thione (382) < N,N-dimethyl-thioacetamide (387) [13] < ϵ-thiocaprolactam (391) [14] < N-ethyl-1,3-imidazolidine-2-thione (397) < thiourea (425) [15]. Hence, the substitution of one hydrogen with a methyl or ethyl in ethylenethiourea produces an increase of Dq, as found by Madan and Sulich [1] on passing from pyrrolidine-2-thione to its N-methyl derivative. Also in our case this trend seems to be in agreement with the electron releasing effect of the substituent.

The β-values, practically the same found for ethylenethiourea, suggest an appreciable orbital overlap, as expected from a largely polarizable donor as the sulphur and, then, locate these ligands at the low end of the nephelauxetic series.

Experimental

N-methyl- and N-ethyl-1,3-imidazolidine-2-thione were prepared according to literature [17, 18].

All the complexes were obtained by refluxing in absolute ethanol the cobalt(II) halide with the ligand (1:2).

The infrared spectra were recorded on a Perkin-Elmer 325 spectrophotometer as KBr discs (4000–400 cm^{-1}) and as Nujol mulls between CsI pellets (450–200 cm^{-1}).

The magnetic susceptibility measurements were carried out by use of the Gouy method at different temperatures (125–260 °K) using liquid air.

The visible spectra in acetone were recorded with a Perkin-Elmer model 402 spectrophotometer. The electronic spectra in the solid state were recorded with a Shimadzu MPS-50L spectrophotometer in the range 4000–27000 cm^{-1}.

The conductivity measurements were carried out with a WTW, LBR type conductivity bridge on 10^{-3} *M* solutions.

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