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A ^1H NMR Fourier Transform Investigation on Cobalt(II) Chloride Complexes with Imidazolidine-2-thione and its N-mono- and N,N'-dialkyl-substituted Derivatives*

FRANCESCO A. DEVILLANOVA, ADOLFO LAI, MAURA MONDUZZI, GIUSEPPE SABA and GAETANO VERANI
Istituto Chimico Policattedra, Via Ospedale 72, 09100 Cagliari, Italy

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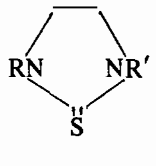
The influence of cobalt(II) chloride on the proton chemical shifts of $RN\cdot CH_2\cdot CH_2\cdot NR'\cdot C{=}S$ *(R,R' = H, Me, Et) has been investigated in* CD_3OD *and* $CDCl_3$ *(1:1 vol). The changes of the chemical shifts and the infrared spectra are indicative of the S-coordination to the metal. The complexes with ligands having R (or R') = H seem to be more stable than the others, in consequence of hydrogen bonding between NH and the halogen. A simplified scheme involving only two equilibria has been proposed, but the accordance between the experimental and calculated data is very poor, thus indicating more complicate equilibria.*

Introduction

Crystalline *pseudo*-tetrahedral complexes obtained by reacting cobalt(II) halides with substituted imidazolidines have been recently reported [1–2]. The ligands considered in these investigations were:



R	R'	
H	Me	ditme
H	Et	ditet
Me	Me	diditme
Et	Et	diditet

and the results were compared with those obtained by Carlin and Holt [3] for imidazolidine-2-thione (R = R' = H; dit). All the complexes were identified as CoL_2X_2 (X = Cl, Br, I) with the ligands bonded to cobalt through the thioketonic sulphur. The crystal field parameters allowed the differentiation of the mono-substituted from the disubustituted ligands, since the former determine higher and the latter lower Dq values than that of the corresponding complex of imidazolidine-2-thione. However, the Dq values were calculated by means of the Tanabe and Sugano equations [4] on the tetrafluoborate complexes of the disubstituted derivatives [2], while, for the N-mono-substituted imidazolidines, the averaged ligand field approximation was used on the CoL_2X_2 complexes to estimate the Dq's for the CoL_4^{2+} species [1].

In order to extend this investigation to liquid solution, we have now carried out a study on the above ligands and dit with cobalt(II) chloride in chloroform-d_1/methanol-d_4 (1:1 vol) by the N.M.R. Fourier transform technique.

Results and Discussion

When cobalt(II) chloride is added to a CD_3OD/$CDCl_3$ solution containing one of the above molecules, larger and larger paramagnetic proton shifts result as the cobalt(II) concentration increases. This clearly means that the metal interacts with the ligand to give coordination compounds in solution. The variations of the chemical shifts $\Delta\delta$ against the cobalt(II)/ligand molar ratio are reported in Figs. 1 and 2 for the five molecules here considered. The investigated short range for the imidazolidine-2-thione (dit) case, see Fig. 1, is due to the low solubility of the cobalt(II) complex.

As can be seen, the side chain protons experience a lower influence of the paramagnetic ion than the endo CH_2, which retain a single signal in the symmetric ligands as expected for the S-coordination, while the mono-substituted ligands obviously show two different resonances arising from their asymmetry (Fig. 2). Figures 1 and 2 also show that the methanol resonances (CHD_2OD) undergo relevant paramagnetic shifts, thus evidentiating cobalt(II)–methanol interaction.

The spectral changes for the ligands in presence of increasing amounts of cobalt(II) are pictured in Fig. 3 for ditet chosen as model compound. It is interesting to point out that cobalt(II) separates the resonances of the two CH_2 in ring, which are very

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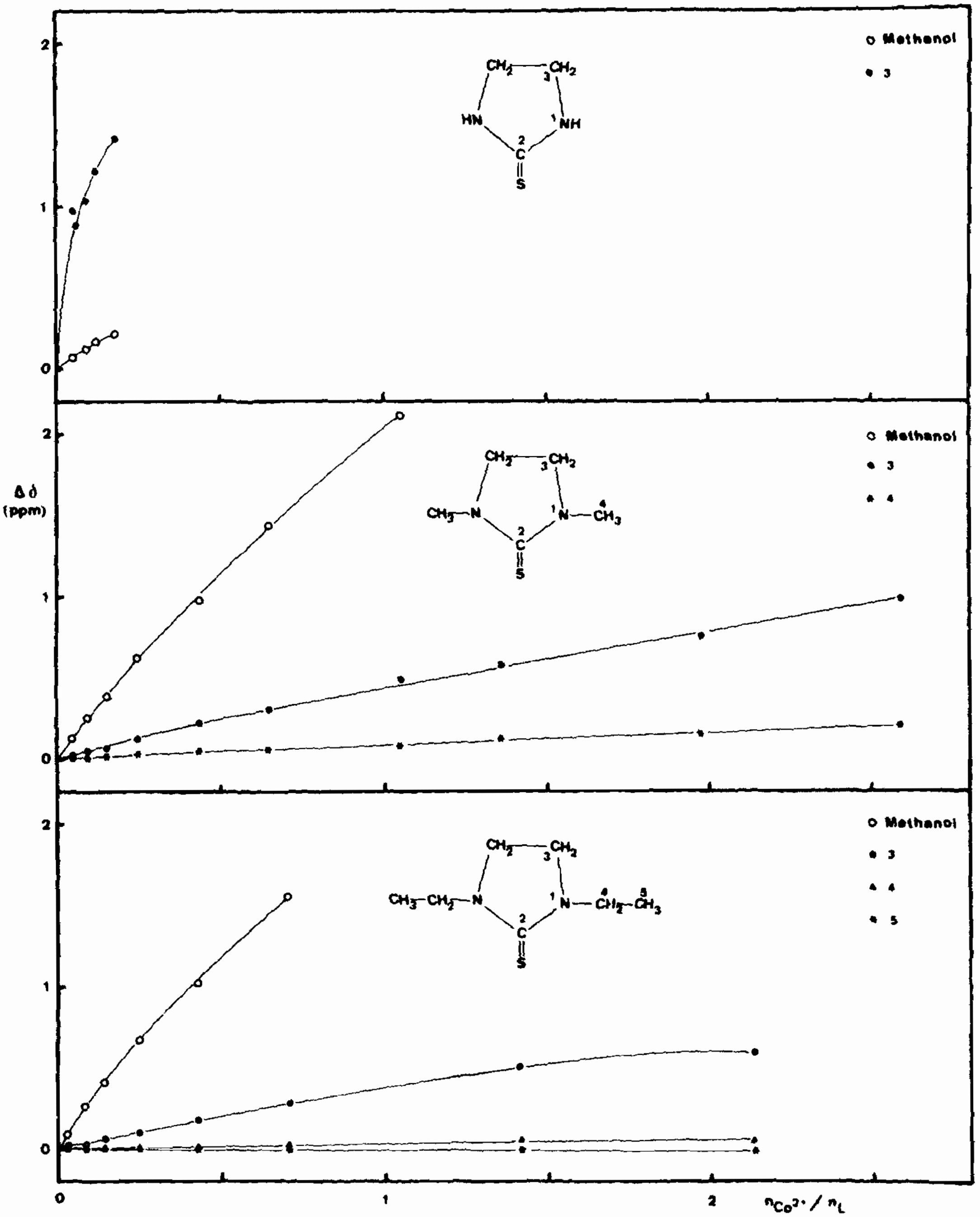

Fig. 1. Changes of $\Delta\delta = (\delta_{obs} - \delta_{free\ ligand})$ for the various proton resonances of the symmetric ligands and methanol.

close in the free ligand, and this shift to low fields is higher for $CH_2(4)$ than for $CH_2(5)$.

Hence the global results show that, also in solution, the coordinative bond in any case occurs through the sulfur atom, as previously seen in solid state [1]. In fact, in the case of the symmetric ligands, a coordination *via* N atom, destroying the symmetry plane perpendicular to the CH_2–CH_2 bond, would differentiate the relative resonances, in contrast with the results. The N-coordination could neither occur for the asymmetric ligands, where steric reasons would require NH rather than N–R as coordinating atom. This possibility is to be discarded both by infrared and n.m.r. data. In fact, the infrared spectra carried out on the cobalt(II) halide complexes with ditet, soluble enough in $CHCl_3$ to be

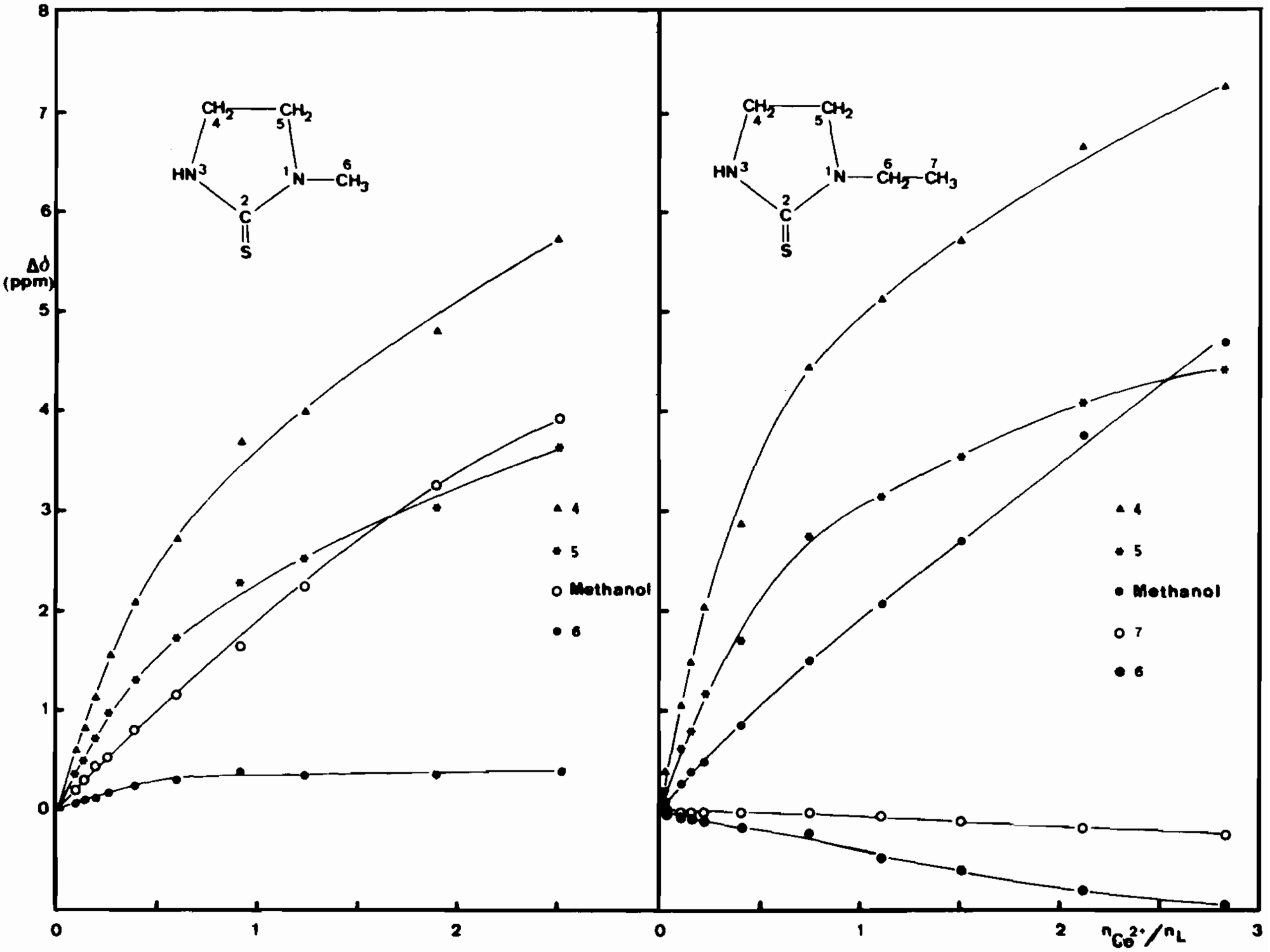

Fig. 2. Δδ changes for the methanol and the proton resonances of the asymmetric ligands.

recorded, show that the ν(CN) vibration shifts by about 30 cm^{-1} towards higher wavenumbers, in agreement with the S-coordination. On the other hand ν(NH) undergoes small shifts with respect to the free ligand*, while the ν(NH) of a quaternary nitrogen would fall below 3000 cm^{-1} [5].

On the other hand, this view is confirmed by p.m.r. spectra, a typical example of which is reported in Fig. 4. In fact the presence of the NH signal in the usual spectral range certainly excludes the N-metal coordination. It is worth noting that the occurrence of the NH resonance, showing a low rate exchange between NH and the methanol, is indicative of hydrogen bonding.

A confirmation of this comes from the infrared spectra of $Co(ditet)_2X_2$ (X = Cl, Br, I), where the ν(NH) progressive shifts to 3265, 3255 and 3235 cm^{-1} for I, Br and Cl respectively point out the involvement of the halogen in this bond. These findings have also been seen for the complexes of the asymmetric imidazolidines with Zn(II), Cd(II), Hg(II) and Cu(I) complexes [7–9].

Turning now to Figs. 1 and 2, we can evidentiate qualitatively the stabilities of the complexes on the basis of the entities of the observed Δδ, which are larger for the ligands having the NH group than for the disubstituted ones. This higher stability should be ascribed to the presence of hydrogen bonding in the former ligands, since neither the negative charge on the sulphur, which is practically the same for all the members of the imidazolidine series [10], nor the steric hindrance of the alkyl groups [11] can be invocated to justify these differences.

In order to obtain quantitative information about the equilibria involved in methanolic solution, the following scheme has been used:

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*In $CHCl_3$ ditet exhibits two strong i.r. absorptions at 3438 and 3230br cm^{-1} due to the free and hydrogen bonded NH respectively. The comparison is obviously referred to the associated one [5].

TABLE. Parameters Obtained by Least Squares Analysis (t = 32 °C).

Ligand	Group[a]	n	S_n[b]	σ_n[c]	K_n[d]	δ_n[d]
dit	$CH_2(3)$	1	0.11/0.11	0.01/0.02	490	<−10.000
		2	0.34/0.30	0.03/0.09	31	>10.000
ditme	$CH_2(4)$	1	0.01/0.01	0.00/0.02	2005	>10.000
		2	0.78/0.16	0.15/0.79	1	245
	$CH_2(5)$	1	0.01/0.01	0.00/0.03	1205	6410
		2	0.84/0.16	0.16/0.82	1	138
ditet	$CH_2(4)$	1	0.20/0.14	0.01/0.40	98	908
		2	0.59/0.08	0.03/0.43	33	524
	$CH_2(5)$	1	0.20/0.14	0.01/0.39	107	587
		2	0.57/0.08	0.03/0.43	34	304
diditme	$CH_2(3)$	1	0.08/0.05	0.00/0.14	459	610
		2	0.53/0.11	0.05/0.57	14	−11
diditet	$CH_2(3)$	1	0.68/0.40	0.02/0.86	12	57
		2	0.22/0.01	0.01/0.05	295	−17

[a] The labels refer to Figs. 1 and 2. [b] $S_n = |C_n|/|Co^{2+}|_t$, where C_n is the complex $CoL_n(MeOH)_{2-n}Cl_2$ and $|Co^{2+}|_t$ is the total cobalt(II) concentration. [c] $\sigma_n = n \cdot |C_n|/|L|_i$, where L_i is the initial concentration of ligand. [d] K_n and δ_n refer respectively to the dissociation constants and the chemical shifts of the complexes.

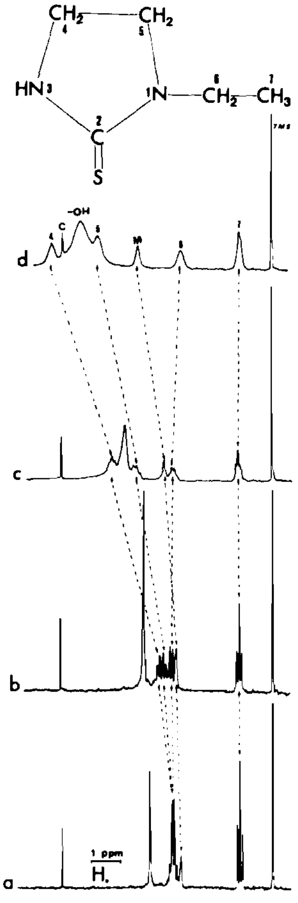

Fig. 3. Evolution of the proton resonances of N-ethyl-imidazolidine-2-thione (ditet) for increasing amounts of cobalt(II) chloride. C and M labels in d spectrum refer to chloroform and methanol respectively.

$$CoL_n(MeOH)_{2-n}Cl_2 + MeOH \underset{}{\overset{K_n}{\rightleftharpoons}} CoL_{n-1}(MeOH)_{3-n}Cl_2 + L$$

where n = 1, 2. This seemed justified by the following considerations:

i) the values of molar conductivities are very low ($<5\ \Omega^{-1}\ cm^2\ mol^{-1}$ in MeOH at room temperature) and hence important contributions of the equilibria involving the removal of the chloride ions can be excluded;

ii) furthermore the complexes show typical u.v. absorptions of tetrahedral cobalt(II)* with molar extinction coefficients sensitive to the amount of ligand concentration, in agreement with the postulated equilibria.

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*The spectral appearance of these complexes consists of three distinct peaks, sensitive to the halide substituent, with the barycentre located near 670 nm for the chloride derivatives.

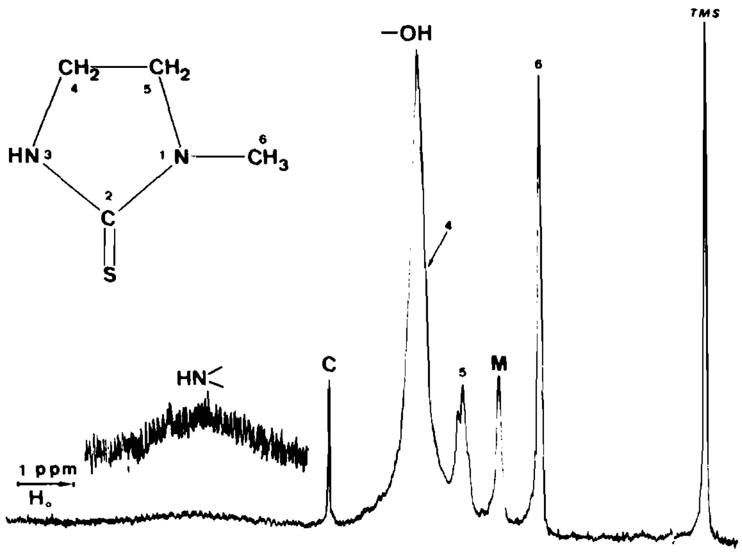

Fig. 4. Spectrum of N-methyl-imidazolidine-2-thione (ditme) in presence of cobalt(II) chloride: |ditme| = 0.1 *M* |$CoCl_2$| = 0.04 *M*.

In order to calculate the K_n's, we have used a program according to Lenkinski's procedure [12]; this program is based on building a map of errors (in a least square sense) whose minimum enables us to find the equilibrium constants (K_1 and K_2) and the intrinsic chemical shifts of the complexes (δ_1 and δ_2) together with their reliability limits. The results obtained for all the ligands are summarized in Table I.

As can be seen, the reliability of the data is very poor. This fact is shown both by the values of S_n and σ_n, which should range between 0.2–0.8, and even more so, by the absence of logicity in K_n and δ_n values. Among all these values, only δ_2 for ditme derivative is reliable and the corresponding K_2 coincide for $CH_2(4)$ and $CH_2(5)$.

It is true that such calculations normally have an intrinsic uncertainty, but in the present case the poverty of the results should be ascribed to the simplified scheme of dissociation, which probably involves further equilibria not considered here. Unfortunately at this stage it is impossible to perform calculations for more complicate systems.

Experimental

All the ligands were prepared according to literature [13–16] and recrystallized from the appropriate solvent.

CD_3OD and $CDCl_3$ were purchased from Merck.

The p.m.r. spectra were run on a Varian FT-80-A spectrometer operating at a nominal frequency of 80 MHz and at a probe temperature of 32 °C. Each spectrum was averaged on 16 transients. The chemical shifts were digitally computed, using TMS as internal reference.

The infrared spectra were recorded on a Perkin-Elmer mod. 325 spectrophotometer in $CHCl_3$ solutions between 1.0 mm KBr windows.

The computations of the dissociation constants and chemical shifts of the ligands in the complexes were performed by means of a program based on Lenkinski's procedure [12] on a 360 I.B.M. computer. This program calculates a map of standard deviations between observed and calculated $\Delta\delta$ (see caption of Fig. 1 for the definition) for various ranges of K_1 and K_2 values. The program also gives saturation factors for the four parameters (K_1, K_2, δ_1 and δ_2).

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