NMR STUDY OF LIGAND EXCHANGE IN SOME METAL DITHIOCARBAMATES

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The ^{1}H-NMR spectroscopy was employed to study solutions of the dithiocarbamates of Cr(III), Fe(III), Co(III), Ni(II), Cu(II) and Zn(II) in carbon disulphide. It was confirmed that, in spite of the marked thermal stability of these complexes, ligand exchange occurs in solution, where the rate of exchange decreases in the order: Zn(II) $\gg$ Ni(II), Fe(III) $\geqq$ Cu(II) $\gg$ Co(III), Cr(III). The exchange practically does not occur in Co(III) and Cr(III) complexes.

The complexes of metals with N,N-disubstituted dithiocarbamic acids are well known and for many their spectral, electrochemical, structural and biochemical properties have been described[1-3]. These anions form stable, generally intensely coloured complexes with transition metals, most frequently with MS_4 or MS_6 chromophores (M-metal, S-sulphur atom from the dithiocarbamate ligand). The complexes are marked by high stability and low solubility in polar solvents. Because of these properties they have found wide use in analytical chemistry[2] and recently it was found that they can be separated and determined by gas chromatography[4,5].

In a study of the properties of dithiocarbamate complexes by the liquid chromatographic method in our laboratory it was found that in nonaqueous solutions an exchange reaction occurs between various complexes of dithiocarbamic acids[6]. In a more detailed study of the dithiocarbamate solutions in connection with the existence of ligand exchange in dithiocarbamate complexes, the ^{1}H-NMR technique was employed.

In the past, NMR spectroscopy has been used primarily for studying the structure of various dithiocarbamates[7], intramolecular processes in transition metal complexes (optical inversion, *cis-trans* isomerization)[8] and hyperfine interactions between unpaired electrons and protons in the dithiocarbamates of Fe(III), Cr(III) and Mn(III) (ref.[9]). Que and Pignolet[8] mentioned the formation of mixed complexes of Fe(II), Fe(III), Fe(IV), V(III) and Ga(III) in a study of the intramolecular processes in octahedral complexes with dicarbamate ligands.

EXPERIMENTAL

The complex compounds Fe(III), Ni(II), Cu(II) and Zn(II) with the ligands $(CH_3)_3NCS_2^-$, $C_2H_5)_2NCS_2^-$, $(C_3H_7)_2NCS_2^-$, $(C_4H_9)_2NCS_2^-$, $(iC_3H_7)(CH_3)NCS_2^-$ and $(iC_4H_9)_2NCS_2^-$ (for Fe(III)) and with the ligands $(iC_3H_7)(CH_3)NCS_2^-$ and $(iC_4H_9)_2NCS_2^-$ (with the other metals) were prepared by the reaction of the appropriate cations with the sodium salts of the dithiocarbamic acids. The dithiocarbamates of Cr(III) were prepared according to ref.[10]. The compounds were recrystallized from a chloroform–ethanol solution and their purity was controlled by elemental analysis (Table I) and on the basis of their NMR spectra.

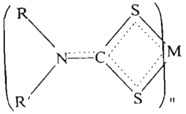
The samples were prepared by mixing carbon disulphide solutions of the appropriate dithiocarbamates in molar ratios of 1 : 1 so that the resultant concentration of the original complexes was approximately 10^{-2}M. The solution temperature was 30°C.

The ^{1}H-NMR spectra were obtained using an 80 MHz NMR instrument BS 474 from Tesla and some systems were measured on a Varian XL-100 instrument (100 MHz).

The chemical shifts of the Fe(III), Ni(II), Zn(II) and Co(III) dithiocarbamates are listed in Table II.

RESULTS AND DISCUSSION

It was found that the ^{1}H-NMR technique is suitable for following the exchange reactions of the dithiocarbamate ligands of metals and that the chemical shifts of these substances are strongly dependent on the character of the central atom, as follows from the structure of dithiocarbamate complexes:



The screening of the protons on the R and R′ radicals, i.e. their diamagnetic chemical shifts, depends on the participation of the lone electron pair on the nitrogen atom in the conjugation with the C=S bond[11]. In complexes with a paramagnetic centre, a paramagentic shift resulting from hyperfine interactions of an unpaired electron with a proton can also be observed. The necessary condition for observation of an NMR signal for these complexes is the validity of the relationship $T_1^{-1} \gg A$, where T_1 is the spin-lattice relaxation time of the electron and A is the hyperfine interaction constant. This condition is very favourable for Fe(III) dithiocarbamates, because the rapid change of equilibrium spin states $^6A_1 \rightleftharpoons {}^2T_2$ considerably shortens the spin-lattice relaxation time[12]. The relaxation time for Cu(II) and Cr(III) complexes is not as favourable.

In a study of ligand exchange, $(iC_3H_7)(CH_3)NCS_2^-$ and $(iC_4H_9)_2NCS_2^-$ ligands were found to be most suitable, as the chemical shifts primarily of the α-protons are strongly dependent on the nature of the central atom, the spectra are first order and the signals of the individual complexes do not overlap (Table II). With Fe(III) complexes, in addition to the ligands mentioned above, the exchange of $(CH_3)_2NCS_2^-$, $(C_2H_5)_2NCS_2^-$, $(C_3H_7)_2NCS_2^-$ and $(C_4H_9)_2NCS_2^-$ ligands was also studied.

TABLE I

Results of Elemental Analysis of Some Dithiocarbamates[a]

Complex	C	H	N	Metal
$Cr((iC_3H_7)(CH_3)NCS_2)_3$	35·21 (36·26)	5·94 (6·07)	8·17 (8·46)	10·10 (10·46)
$Co((iC_3H_7)(CH_3)NCS_2)_3$	34·73 (35·76)	5·76 (6·00)	8·08 (8·34)	11·70 (11·70)
$Cu((iC_4H_9)_2NCS_2)_2$	45·00 (45·78)	7·31 (7·68)	5·90 (5·98)	13·40 (13·45)
$Ni((iC_3H_7)(CH_3)NCS_2)_2$	33·12 (33·81)	5·60 (5·67)	7·50 (7·89)	16·43 (16·53)
$Zn((iC_4H_9)_2NCS_2)_2$	45·12 (45·60)	7·30 (7·65)	5·85 (5·91)	13·60 (13·79)
$Fe((C_2H_5)_2NCS_2)_3$	36·76 (35·98)	5·98 (6·04)	8·37 (8·39)	11·10 (11·15)
$Fe((iC_3H_7)(CH_3)NCS_2)_3$	35·34 (35·98)	6·03 (6·04)	8·31 (8·39)	11·20 (11·15)

[a] Calculated values are given in brackets.

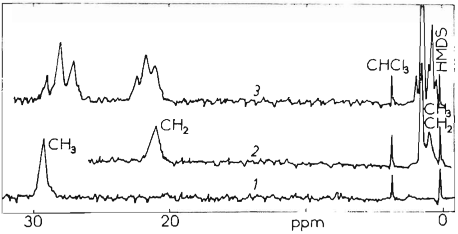


FIG. 1

The 80 MHz ^{1}H-NMR Spectra of Carbon Disulphide Solutions of $Fe((CH_3)_2NCS_2)_3$ (*1*), $Fe((C_3H_7)_2NCS_2)_3$ (*2*) and of the Systems $Fe((CH_3)_2NCS_2)_3$–$Fe((C_3H_7)_2NCS_2)_3$ after Establishment of Equilibrium (*3*)

Solution temperature, 30°C.

TABLE II

The ^{1}H-NMR Chemical Shifts δ and Interaction Constants of the Dithiocarbamates of Some Metals[a]

Complex	δ_A	δ_B	δ_C	δ_D	J_{AB} Hz	J_{BC} Hz
$Ni((iC_4H_9)_2NCS_2)_2$	3·33^{b}	2·10^{c}	0·91^{b}		7·6	6·5
$Ni((iC_3H_7)(CH_3)NCS_2)_2$	4·78^{d}	1·20^{b}			6·7	
	2·91^{e,f}					
$Zn((iC_4H_9)_2NCS_2)_2$	3·60^{b}	2·35^{c}	0·96^{b}		7·5	6·4
$Zn((iC_3H_7)(CH_3)NCS_2)_2$	5·19^{d}	1·23^{b}			6·7	
	3·20^{e,f}					
$Co((iC_4H_9)_2NCS_2)_3$	3·41^{b}	2·14^{c}	0·92^{b}		7·5	6·2
$Co((iC_3H_7)(CH_3)NCS_2)_3$	4·81^{d}	1·19^{b}			6·5	
	3·12^{e,f}					
$Fe((CH_3)_2NCS_2)_3$	58·5					
$Fe((C_2H_5)_2NCS_2)_3$	46·8	0·9				
$Fe((C_2H_5)_2NCS_2)_3$^{g}	40·6	0·9				
$Fe((C_3H_7)_2NCS_2)_3$	42·1	1·5	2·8			
$Fe((C_4H_9)_2NCS_2)_3$	43·4	2·9	1·3	1·3		
$Fe((iC_3H_7)(CH_3)NCS_2)_3$	50·7	3·0				
$Fe((iC_4H_9)_2NCS_2)_3$	29·8	3·9	2·2			

[a] In CS_2 at 30°C, chemical shifts δ in ppm units relative to the signal of tetramethylsilane. Indexes A, B, C and D indicate the protons on the hydrocarbon chain in the α, β, γ and δ positions relative to the nitrogen atom; [b] doublet; [c] nonet; [d] septet; [e] singlet; [f] N-methyl; [g] $CDCl_3$ solvent.

TABLE III

Summary of the Course of Ligand Exchange Between Dithiocarbamate Complexes[a]

Complex	CrL_3	FeL_3	CoL_3	NiL_2	CuL_2	ZnL_2
FeL'_3	n	s	n	s	s	r
NiL'_2	n	s	n	—	s	r
ZnL'_2	n	r	n	r	r	—

[a] Meaning of symbols: r rapid exchange, s slow exchange, n no exchange; L,L′-dithiocarbamate ligands.

When mixing two diamagnetic complexes having identical central atoms (*e.g.* $Ni((iC_3H_7)(CH_3)NCS_2)_2$ and $Ni((iC_4H_9)_2NCS_2)_2$), only the NMR signals of the original complexes were observed and no further signals appeared, even after a prolonged period of time. Assuming that the mixed complex $Ni((iC_3H_7)(NCS_2)\,.\,((iC_4H_9)_2NCS_2)$ is formed, as was confirmed by liquid chromatography[6], then this complex yields signals identical with those of the original complex. The large distance between the ligands in the mixed complex leads to an immeasurably small change in the chemical shifts.

The complexes of Fe(III) behave differently, as the paramagnetic centre leads to large paramagnetic shifts primarily of the protons in the α-position relative to the

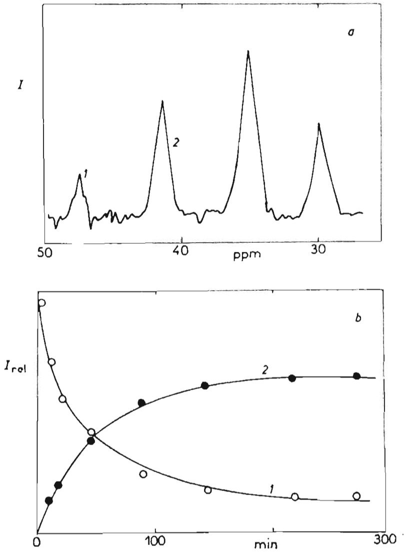


FIG. 2

Methylene Signal Region for the System $Fe((C_2H_5)_2NCS_2)_3$–$Fe((iC_4H_9)_2NCS_2)_3$ after Establishment of Equilibrium A *a* and Dependence of the Relative Intensity of the Signals (*1*) and (2) on Time for This System (*b*)

80 MHz spectra measured in CS_2 at 30°C.

nitrogen atom (Table II). These shifts are strongly dependent on the character of the ligand and thus it was assumed that every change in the coordination sphere of the complex should appear as a change in the chemical shift.

It was found that, new signals corresponding to the mixed complexes appeared on the spectra in addition to the signals of the original complexes when mixing two complexes of Fe(III). The most marked changes were observed in the region of the signals of the α-protons, while in the regions of other signals the new signals more or less overlap with the original ones (Fig. 1).

The following equilibrium is formed in solution:

$$\mathrm{FeL_3} + \mathrm{FeL'_3} \rightleftharpoons \mathrm{FeL_2L'} + \mathrm{FeLL'_2}, \qquad (A)$$

where L and L′ are dithiocarbamate ligands. After mixing two complexes, three different signals for the ligands L in the FeL_3, FeL_2L' and $FeLL'_2$ complexes and, analogously, three signals for the L′ ligand in the FeL'_3, $FeLL'_2$ and FeL_2L' complexes were observed.

The intensity of the signals of the mixed complexes increase in time in contrast to the intensity of the original signals, which decreases. Equilibrium is formed after approximately two hours. The time course of the signal intensity of the methylene protons in the $Fe((C_2H_5)_2NCS_2)_3$–$Fe((iC_4H_9)_2NCS_2)_3$ system is depicted in Fig. 2. Here only four signals were observed in the region of signals of the α-protons, which can be explained by overlapping of signals of mixed complexes. Four poorly resolved signals were also observed for the $Fe((C_2H_5)_2NCS_2)_3$–$Fe((C_3H_7)_2NCS_2)_3$ system. The $Fe(iC_3H_7)(CH_3)NCS_2)_3$–$Fe((iC_4H_9)_2NCS_2)_3$ and $Fe(iC_3H_7)(CH_3)NCS_2)_3$–$Fe((C_4H_9)_2NCS_2)_3$ systems yield similar spectra to those of the $Fe((CH_3)_2NCS_2)_3$–$Fe((C_3H_7)_2NCS_2)_3$ system (Fig. 1).

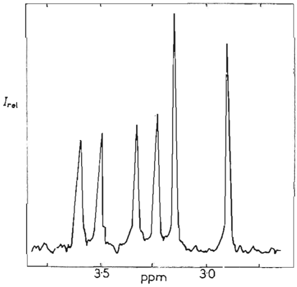


FIG. 3

Part of the 80 MHz ^{1}H-NMR Spectra of the $Zn((iC_4H_9)_2NCS)_2$–$Ni((iC_3H_7)(CH_3)$ . . $NCS_2)_2$ System

Solvent CS_2, temperature 30°C.

Ligand exchange between divalent metals is much faster than for Fe(III), Co(III) and Cr(III). This apparently depends on planar coordination of divalent metals where – analogously to the solid state of aggregation – the ligands can interact in the axial direction and thus the S_{N2} mechanism of ligand exchange is possible.

Ligand exchange between Ni(II) and Zn(II) dithiocarbamates is very rapid and equlibrium is established practically immediately after solution mixing. Fig. 3 depicts the spectrum of the region of the signals of the α-protons of the $Ni((iC_3H_7)(CH_3) . NCS_2)_2$–$Zn((iC_4H_9)_2NCS_2)_2$ system, from which it follows that the $(iC_3H_7)CH_3 . NCS_2^-$ and $(iC_4H_9)_2NCS_2^-$ ligands are bound to both nickel and zinc atoms, *i.e.* that ligand exchange occurred. Identical spectra were obtained for the $Ni((iC_4H_9)_2 . NCS_2)_2$–$Zn((iC_3H_7)(CH_3)NCS_2)_2$ system.

Under the conditions for measuring the NMR spectra of diamagnetic dithiocarbamates, copper(II) dithiocarbamate yielded weak, very broad signals, where the signals of the α-protons could not be recorded.

In mixtures of the dithiocarbamates of Ni(II) and Zn(II) or Cu(II), only the signals of the α-protons of diamagnetic dithiocarbamates were observed in the chemical shift region 2·5 – 3·5 ppm. It was found that ligand exchange between Cu(II) and Ni(II) complexes is slower (equilibrium is formed after about 1 hour) than exchange between Cu(II) and Zn(II) complexes, where equilibrium is formed immediately after complex mixing.

It was further found that ligand exchange between Fe(III) and Ni(II) complexes is much slower than exchange between Fe(II) and Zn(III) complexes. In the former case, equilibrium was formed after about one hour, in the latter immediately after mixing. Signals corresponding to mixed Fe(III) complexes also appear in the spectra.

Ligand exchange between dithiocarbamates of Co(III) or Ni(II) and Zn(II) is very slow; the ligand exchange does not appear on the NMR spectra after two months after mixing the complexes. These observations are in agreement with the general inertness of the Co(III) and Cr(III) complexes towards changes in their coordination sphere, as the optical inversion through trigonal shift proceeds very slowly[8].

The relative rates of ligand exchange between dithiocarbamate complexes are listed in Table III. It can be stated on the basis of the results obtained that the rate of ligand exchange for the studied metals decreases in the following order:

$$\mathrm{Zn(II)} \gg \mathrm{Ni(II)},\ \mathrm{Fe(III)} \geqq \mathrm{Cu(II)} \gg \mathrm{Co(III)},\ \mathrm{Cr(III)}.$$

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REFERENCES

1. Thorn G. D., Ludwig R. A.: *The Dithiocarbamates and Related Compounds.* Elsevier, Amsterdam 1962.
2. Magee R. J.: Rev. Anal. Chem. *1*, 333 (1973).

3. Halls D. J.: Microchim. Acta *1969*, 62.
4. J. Masaryk J., Krupčík J., Garaj J., Košík M.: J. Chromatogr. *115*, 256 (1975).
5. Krupčík J., Garaj J., Holotík Š., Oktavec D., Košík M.: J. Chromatogr. *112*, 189 (1975).
6. Liška O., Guichon G., Collin H.: J. Chromatogr. *171*, 145 (1979).
7. Johnson B. F. G., Al-Obaidi K. H., McCleverty J. A.: J. Chem. Soc. *A 1969*, 1668.
8. Que L., jr, Pignolet L. H.: Inorg. Chem. *13*, 351 (1974).
9. Golding R. M., Lukeman B. D., Sinn E.: J. Chem. Phys. *56*, 4147 (1972).
10. Tulyupa F. M., Zheltobryuch L. P.: Ukr. Khim. Zh. *1976*, 72.
11. Nikolov G. S.: Inorg. Nucl. Chem. Lett. *7*, 1213 (1971).
12. Zajev E. E., Larionov S. V., Molin J. N.: Dokl. Akad. Nauk USSR *168*, 341 (1966).

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