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LIQUID CHROMATOGRAPHY OF METAL COMPLEXES OF N-DISUBSTITUTED DITHIOCARBAMIC ACIDS

II. IDENTIFICATION OF NICKEL(II) BISDIALKYLDITHIOCARBAMATE MIXED-LIGAND COMPLEXES

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SUMMARY

In separating a mixture of two symmetrical nickel(II) bisdialkyldithiocarbamates by high-performance liquid chromatography, the formation of a third compound was observed for every pair of complexes with different N-alkyl substituents analysed. The assumption that each of these third compounds is a mixed-ligand complex was verified by two-dimensional thin-layer chromatography, determination of molecular weight and elemental analysis. The complexes are not stable after separation and decompose immediately in chloroform solution, generating a ternary equilibrium mixture of the mixed-ligand complex and the two original symmetrical complexes.

INTRODUCTION

In Part I (ref. 1), the influence of the size and type of N-alkyl substituents and of the elutropic strength of the mobile phase on the capacity ratios of eleven nickel(II) bisdialkyldithiocarbamate (DTC) complexes was examined. This information was useful in selecting the optimal conditions for the separation of mixtures of these complexes by high-performance liquid chromatography (HPLC). We noticed, however, that every mixture of two different complexes gave three chromatographic peaks, and we assumed that a mixed-ligand complex of the type L_1-Ni-L_2 is formed upon mixing solutions of L_1-Ni-L_1 and L_2-Ni-L_2 .

Mixed complexes that bond two or more different ligands on a central metallic atom are well known. Their formation is caused mainly by the exchange of ligands as the result of dissociation of more symmetrical complexes in a polar solvent. Ligand exchange in a non-polar solvent is, however, less frequent. Many workers have

reported ligand exchange in metal complexes of DTC acids or similar compounds²⁻¹¹. The exchange reactions in acetone, acetonitrile, CD_2Cl_2 or $CDCl_3$ were studied by a.c. voltametry and NMR and PMR spectrometry. Attempts to isolate the mixed-ligand complexes were successful in only a few instances.

Basolo and Pearson¹² explained the substitution reactions of complex compounds where ligand exchange takes place in non-polar solvents.

An explicit method for the identification of the mixed-ligand complex formed would provide its physico-chemical and X-ray structural data after its isolation in the pure solid state. Isolation of the mixed-ligand complex was attempted by conventional preparative chromatography on silica gel and alumina columns as well as by preparative thin-layer chromatography (TLC). As compound mainly studied was the complex formed by ligand exchange between nickel(II) bisdiethyldithiocarbamate and nickel(II) bisdihexyldithiocarbamate. These two symmetrical complexes are easy to crystallize and it was expected that the mixed-ligand complex would also crystallize. The higher alkyl derivatives are amorphous.

EXPERIMENTAL

Conventional preparative chromatography was performed on glass columns packed with silica gel (LS 5/40, 80–100 μm , 20 \times 1.8 cm). The silica gel was activated at 120° for 1 h and filled into a glass column as a suspension in *n*-hexane. Another column with the same dimensions was packed with alumina for chromatographic use (Lachema, Brno, Czechoslovakia). The alumina was activated at 350° for 1 h and the column was filled by a similar technique. Commercial plates coated with Silufol silica gel (15 \times 15 cm) (Kavalier, Sklářny, Czechoslovakia) were used for TLC. The plates were washed with chloroform and activated at 120° for 1 h before use. The development time for the TLC plates was *ca.* 20 min at room temperature. The separated spots of the complexes were evaluated with an ERI 10 photodensitometer (Carl Zeiss, Jena, G.D.R.). The peak areas were measured with an Amsler polar planimeter.

For preparative TLC, samples of an equimolar mixture of the two symmetrical complexes were applied on the plate, side by side (25 spots, each 50 μl , 0.05 *M* solution of both complexes). Five plates were developed simultaneously. After development, the zones corresponding to the mixed complex were cut out, the complex was extracted with chloroform under an inert atmosphere and the solvent was removed in a rotary vacuum evaporator.

The molecular weights of the normal complexes and the isolated mixed-ligand complex were determined by vapour-phase osmometry on chloroform solutions, using an apparatus built at the Institute of Macromolecular Chemistry of the Czechoslovak Academy of Sciences (Prague). A chloroform solution of di(2-ethylhexyl) sebacate (M.W. 426) was used as a comparative standard. The measurements were made at 27°, using solutions of the standard and of the DTC complexes with concentrations of 5, 10 and 20 $mg \cdot cm^{-3}$. The molecular weights of the complexes were evaluated from a calibration graph.

Carbon, hydrogen and nitrogen contents were determined using a Model 1102 elemental analyser (Carlo Erba, Milan, Italy). Sulphur was determined by the Burger-Zimmermann method¹³.

The complexes used [nickel(II) bisdiethyl- up to bisdioctyl-DTC] were

prepared by the usual procedure¹⁴ in our laboratory. The complexes were recrystallized three times from chloroform and their purity was controlled by measuring the melting point, elemental composition and UV spectra.

All solvents were of analytical-reagent grade (Lachema) and were dried over anhydrous magnesium perchlorate and redistilled before use.

RESULTS AND DISCUSSION

Attempts to isolate the mixed-ligand complex nickel(II) diethyl-DTC dihexyl-DTC by conventional preparative column chromatography, with the use of silica gel and alumina as adsorbent and chloroform-cyclohexane mixtures as mobile phase, were unsuccessful. Three coloured zones, corresponding to the two original complexes and the mixed-ligand complex, were formed, but they were not well separated and the middle zone, corresponding to the mixed-ligand complex, disappeared very quickly. This suggests that the complex formed is not stable and decomposes into the original symmetrical complexes after separation. We could not prevent the decomposition of the mixed-ligand complex by accelerating the separation by pressurization of the mobile phase.

Because TLC allows faster separations, we used it for the preparative separation of the complex mixture. Chloroform, tetrachloromethane, *n*-heptane, cyclohexane and mixtures of these solvents were studied as the mobile phase. Chloroform-cyclohexane (3:4, v/v) proved the most suitable for the separation of nickel(II) bisdialkyl-DTC complexes (Figs. 1 and 2, curve 4) and was used exclusively in further work.

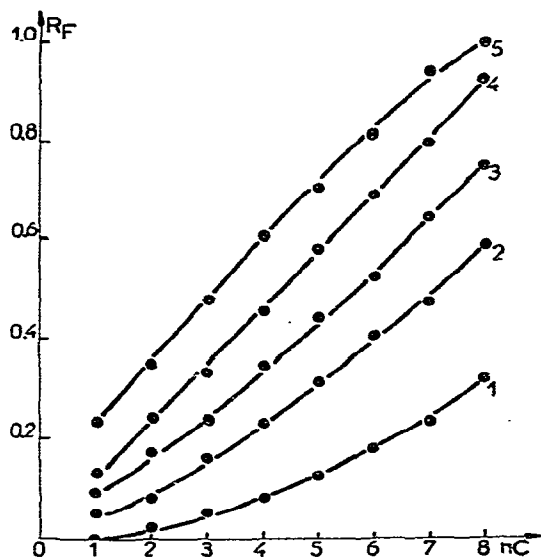


Fig. 1. R_f values versus number of carbon atoms in alkyl chain of Ni(II) bisdialkyl-DTC complexes. TLC on Silufol silica gel plate. Mobile phase: chloroform-cyclohexane mixtures containing $x\%$ (v/v) of chloroform. Curves: 1, $x = 33.3$; 2, $x = 37.5$; 3, $x = 40.0$; 4, $x = 42.8$; 5, $x = 46.1$.

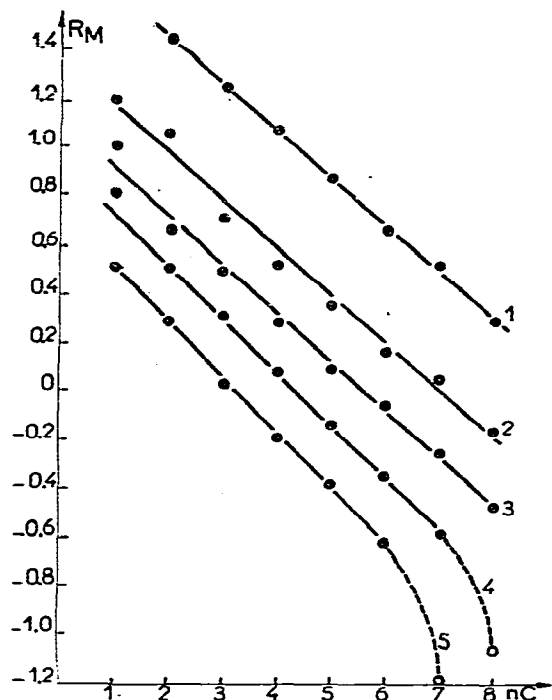


Fig. 2. R_M versus number of carbon atoms in alkyl chain of Ni(II) bisdialkyl-DTC complexes. Conditions and curves as in Fig. 1.

We investigated all combinations of pairs of complexes having substituents from N-diethyl up to N-dioctyl, and we always observed the formation of an intermediate spot representing a mixed-ligand complex. As in the HPLC analysis of nickel(II) bisdialkyl-DTC complexes¹, we found that the larger the difference between the numbers of carbon atoms in the two ligands, the larger was the deviation of the R_F value of the mixed complex from the value predicted by the rule of additivity of group contributions. Fig. 3 shows the R_F values of the symmetrical C_2 - C_8 DTC complexes and of some mixed-ligand complexes.

We chose the combination diethyl-dihexyl-DTC to ascertain the identity of the mixed complex. Equimolar volumes of the two symmetrical complexes and of their equimolar mixture were applied on the same Silufol plate. The brown-green spots of the complexes observed after development were scanned and the peak areas measured.

The total area of the spots in the chromatogram of the mixture is almost identical with the sum of the areas of the two spots obtained with the two pure substances (Table I); the areas of the three spots of the mixture are in the ratio 1:1:1.

By preparative TLC we isolated 38 mg of microcrystalline product. This product was dried under a pressure of 0.01 Torr above phosphorus pentoxide at 60°. This procedure also removed chloroform, which can form an adduct with metal DTC complexes^{15,16}. The results of the elemental analysis indicate a structure corresponding to the mixed-ligand complex (Table II). However, the HPLC and TLC results indicated that the isolated product is a mixture of three substances, of which

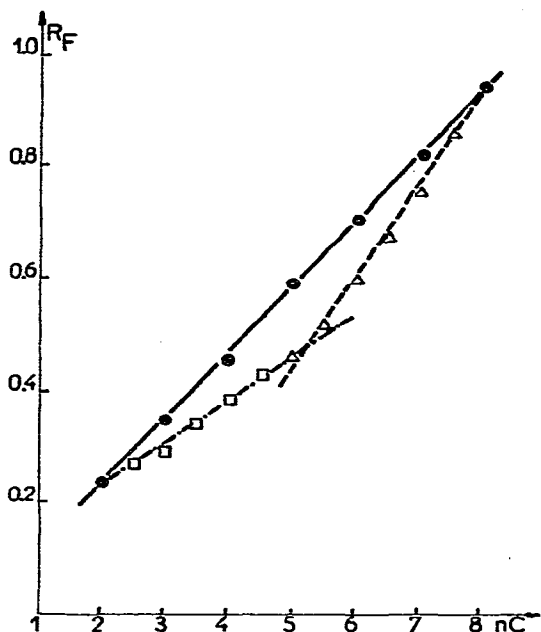


Fig. 3. Relationship between R_F values and number of carbon atoms in alkyl chain of Ni(II) bisdialkyl-DTC complexes and mixed-ligand complexes. TLC on Silufol silica gel plate. Mobile phase: chloroform-cyclohexane (3:4, v/v). Curves: ●, Ni(II) bisdialkyl-DTC (alkyl = ethyl, propyl, ..., octyl); □, mixed-ligand complexes Ni(II) $R_2R'_2$ -DTC (R = ethyl; R' = propyl, butyl, pentyl, hexyl, heptyl); △, mixed-ligand complexes Ni(II) $R_2R'_2$ -DDC (R = octyl; R' = ethyl, propyl, butyl, pentyl, hexyl, heptyl).

TABLE I

PHOTOMETRY OF SPOTS OF NICKEL(II) BISDIALKYL-DTC COMPLEXES ON SILUFOL PLATES

The area of each spot scanned was measured with an Amsler polar planimeter; each value is the mean of ten measurements.

Amount of each complex (μ mole)	Sum of areas of spots of two symmetrical complexes (cm^2)	Sum of areas of spots of two symmetrical complexes and the third complex (cm^2)	Difference (%)
0.1	2.07	1.99	-3.86
0.2	3.89	3.93	+1.03
0.3	7.03	6.98	-0.71
0.4	7.52	7.48	-0.53
0.5	8.26	8.30	+0.48

TABLE II

ELEMENTAL ANALYSIS OF THE MIXED-LIGAND COMPLEX NICKEL(II) DIETHYL-DTC DIHEXYL-DTC ($C_{18}H_{36}N_2S_4Ni$), MOL. WT. 467.47

	C (%)	H (%)	N (%)	S (%)
Calculated	46.25	7.76	5.99	27.44
Found	46.53	7.70	5.87	27.23

two are identical with the original symmetrical complexes. All attempts to prepare crystals of the mixed-ligand complex by preparative TLC were unsuccessful.

The elemental analysis of the isolated product showed that the carbon, hydrogen, nitrogen and sulphur contents of the mixed-ligand complex are the same as those of the equilibrium mixture.

Both the instability of the mixed-ligand complex and its identity were verified by two-dimensional TLC. A mixture of nickel(II) bisdiethyl- and bisdiethyl-DTC was separated on a Silufol plate and three spots were formed. After development of the plate in the first direction, it was pulled out of the liquid solvent and left for at least 20–30 min in the chromatographic chamber without contact with the mobile phase. During this period the solvent evaporated slowly. Then the plate was dried under a stream of warm air and the development in the second direction was performed in the same mobile phase system. The spot of the mixed-ligand complex was again separated into three spots (Fig. 4). Because the decomposition of the unsymmetrical complex proceeds slowly during TLC analysis, slight traces of symmetrical complexes making a continuous light band appear between the spots. They are not shown on Fig. 4. The positions of the five spots and especially the fact that the two lone spots and the middle spot of the group of three are diagonal on the plate proves that the unknown new compound is the mixed-ligand complex.

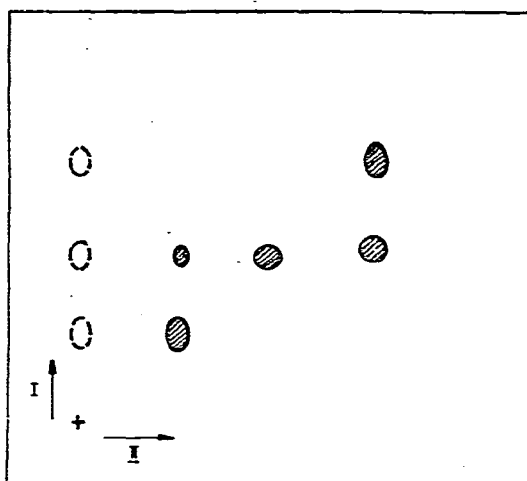


Fig. 4. Two-dimensional separation of a mixture of Ni(II) bisdiethyl- and bisdiethyl-DTC complexes on Silufol silica gel plate. Mobile phase in both directions: chloroform-cyclohexane (3:4, v/v). The middle spot is the mixed-ligand complex.

Finally, it was necessary to exclude the possibility of mixed dimer formation, because some workers have found that metal DTC complexes can exist as dimers not only in the solid phase but also in solution and even in the vapour phase^{17,18}. By determining their molecular weights, it was shown that all of the nickel(II) bisdialkyl-DTC complexes, either symmetrical or in the mixed-ligand form, exist as monomers in chloroform solution (Table III).

TABLE III

DETERMINATION OF MOLECULAR WEIGHT OF NICKEL(II) BISDIALKYL-DTC COMPLEXES

Complex	Molecular weight		Difference (%)
	Calculated	Determined	
Ni(II) bisdiethyl-DTC	467.47	477.7	+2.19
Ni(II) diethyl-DTC dihexyl-DTC*	467.47	496.3	+6.18
		507.5	+8.56

* Compound isolated by preparative TLC.

CONCLUSION

Although the compounds concerned could not be isolated as pure crystals, evidence has been provided to demonstrate the validity of the assumption that the mixed-ligand complexes which are always in equilibrium with mixtures of the symmetrical complexes are formed by ligand exchange between two nickel(II) bisdiethyl-DTC complexes in chloroform solution.

HPLC permits the rapid separation of less stable mixed-ligand complexes and can be used to study their stability and the influence of the type of ligand, temperature, solvent, etc.

The readiness with which equilibrium is achieved makes the analysis of residues of DTC complexes in food a very tedious and challenging task.

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