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## Note

### Liquid chromatography of metal complexes of N-disubstituted dithiocarbamic acids

#### III. High-performance liquid chromatography of bisdialkyl dithiocarbamate complexes of copper(II), cobalt(II), zinc(II) and lead(II)\*

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In a previous paper<sup>1</sup> we described the separation of nickel(II) bisdialkyl dithiocarbamate (DTC) complexes. We investigated the dependence of the capacity ratios on the polarity of the mobile phase and on the number of carbon atoms in the alkyl substituents. The formation of new complexes was observed whenever mixtures of two complexes with different N-alkyl substituents were injected into the column. The new complexes were identified as mixed-ligand complexes<sup>2</sup>.

In this paper we consider the possibility of the separation and identification of DTC complexes of other metals.

## EXPERIMENTAL

All experiments were carried out on a Packard Model 8200 high-performance liquid chromatograph with a UV detector at 254 and 280 nm. A metal column (25 × 0.46 cm) filled with LiChrosorb Si 60 (10 μm) was used. The dialkyl-DTC complexes were synthesized according to the literature<sup>3</sup>. The solid products were recrystallized three times from chloroform, analysed by elemental analysis and characterized by ultraviolet and infrared spectroscopy and by their melting points. Solutions (0.005 M) of DTC complexes in chloroform were used and injected with a 10-μl Hamilton syringe. The mixture was prepared directly in the syringe before injection.

Organic solvents (dichloromethane, chloroform, carbon tetrachloride, cyclohexane, tetrahydrofuran, *n*-pentane and *n*-hexane) were of analytical-reagent grade (Lachema, Brno, Czechoslovakia) and were dried over magnesium perchlorate and redistilled.

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## RESULTS AND DISCUSSION

A number of combinations of organic solvents were investigated, and mixtures of chloroform and dichloromethane with less polar organic solvents were found to be the most suitable.

It should be noted that with other phase systems such as tetrahydrofuran-cyclohexane, tetrahydrofuran-carbon tetrachloride and chloroform-*n*-hexane mixtures, the peaks were considerably distorted and therefore the separation of dialkyl-DTC complexes was not studied with these solvents.

In order to demonstrate the influence of the alkyl chain on the capacity ratios, the values of  $\log k'$  for DTC complexes of cobalt, copper, zinc and lead were plotted against the number of carbon atoms in the alkyl chain bound to the nitrogen atom. In all instances the relationship was linear (Figs. 1-4). For all metals, the highest values of the capacity ratios were obtained for the dimethyl derivatives.

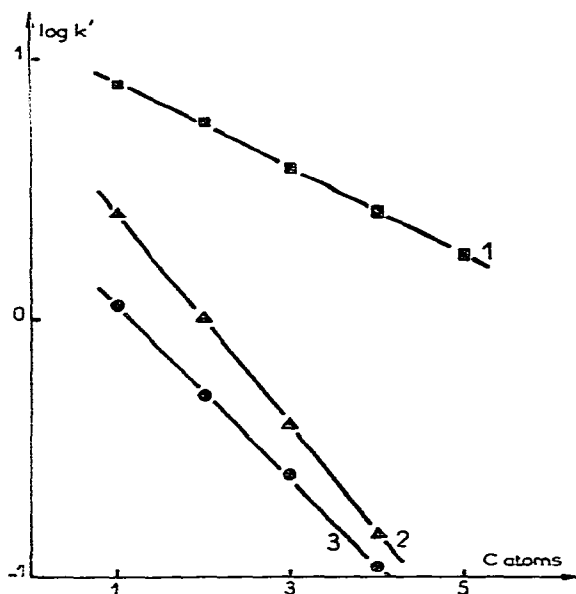


Fig. 1. Dependence of  $\log k'$  on the number of carbon atoms in the alkyl chain of Cu(II) bisdialkyl-DTC complexes. Mobile phase composition: (1) 30% dichloromethane in *n*-pentane; (2) 30% dichloromethane in carbon tetrachloride; (3) 40% dichloromethane in carbon tetrachloride.

Figs. 5-7 demonstrate that the separation of DTC complex mixtures can be achieved by high-performance liquid chromatography (HPLC). In the analysis of mixtures of zinc (II) bisdialkyl-DTC complexes and mixtures of lead (II) bisdialkyl-DTC complexes, it can be seen that in addition to the peaks of the symmetrical complexes used to prepare the sample mixture, peaks of mixed-ligand complexes are also observed. These complexes are formed according to the equation



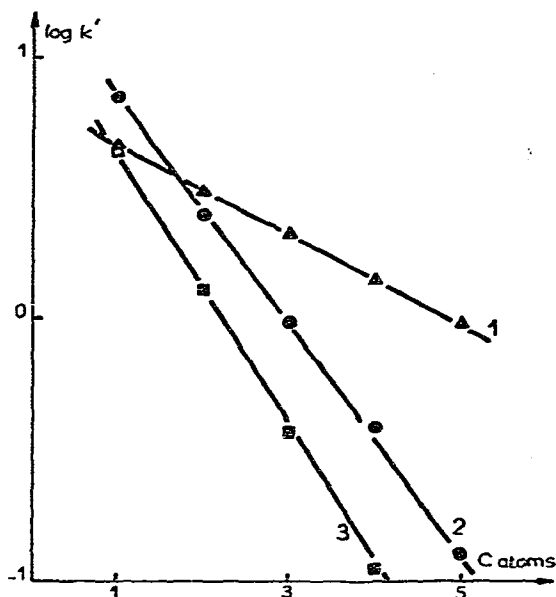


Fig. 2. Dependence of  $\log k'$  on the number of carbon atoms in the alkyl chain of Co(II) bisdialkyl-DTC complexes. Mobile phase composition: (1) 70% dichloromethane in *n*-pentane; (2) 40% dichloromethane in carbon tetrachloride; (3) 60% dichloromethane in carbon tetrachloride;

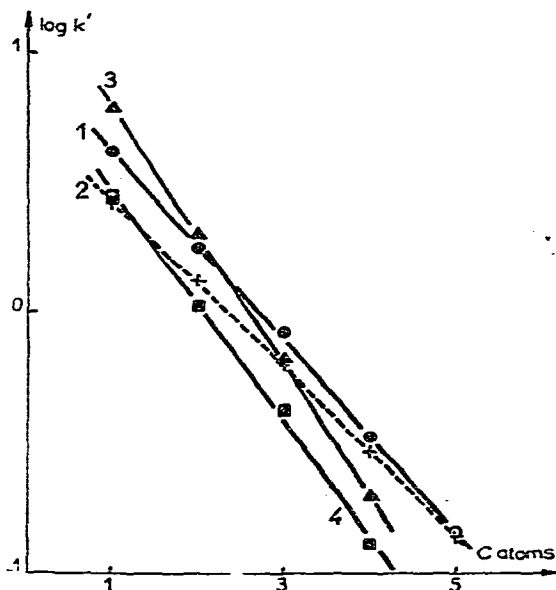


Fig. 3. Dependence of  $\log k'$  on the number of carbon atoms in the alkyl chain of Zn(II) bisdialkyl-DTC complexes. Mobile phase composition: (1) 30% dichloromethane in carbon tetrachloride; (2) 70% dichloromethane in *n*-pentane; (3) 10% chloroform in cyclohexane; (4) 40% dichloromethane in carbon tetrachloride.

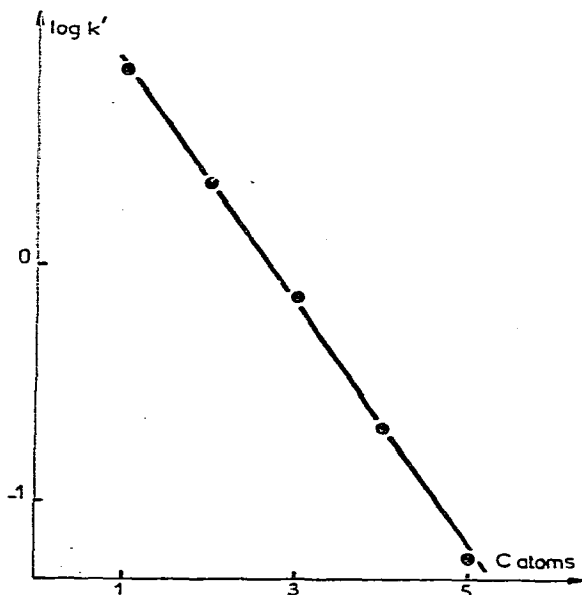


Fig. 4. Dependence of  $\log k'$  on the number of carbon atoms in the alkyl chain of Pb(II) bisdialkyl-DTC complexes. Mobile phase composition: 10% chloroform in cyclohexane.

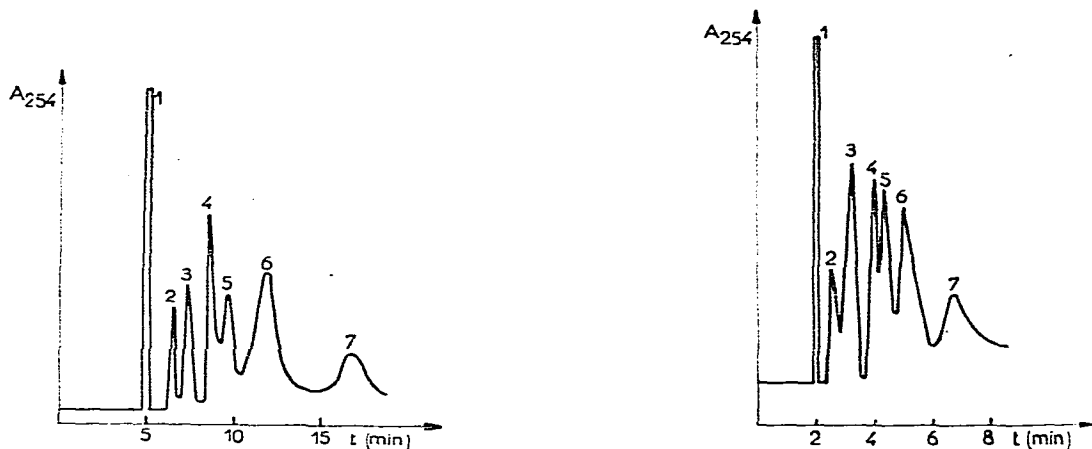


Fig. 5. Separation of Zn(II) bisdialkyl-DTC complexes. Solvent: 10% chloroform in cyclohexane. Column:  $25 \times 0.46$  cm, LiChrosorb SI 60, particle size  $10 \mu\text{m}$ . Solvent velocity,  $0.08 \text{ cm} \cdot \text{sec}^{-1}$ ; pressure drop, 2.75 MPa. Peaks: 1 = inert peak; 2 = Zn(II) bisdibutyl-DTC; 3 = mixed-ligand complex, Zn(II) dipropyl-DTC dibutyl-DTC; 4 = Zn(II) bisdipropyl-DTC; 5 = Zn(II) diethyl-DTC dibutyl-DTC; 6 = Zn(II) diethyl-DTC dipropyl-DTC; 7 = Zn(II) bisdiethyl-DTC.

Fig. 6. Separation of Pb(II) bisdialkyl-DTC complexes. Solvent: 10% chloroform in cyclohexane. Column as in Fig. 5. Solvent velocity,  $0.19 \text{ cm} \cdot \text{sec}^{-1}$ ; pressure drop, 5.39 MPa. Peaks: 1 = inert; 2 = Pb(II) bisdibutyl-DTC; 3 = Pb(II) dipropyl-DTC dibutyl-DTC; 4 = Pb(II) bisdipropyl-DTC; 5 = Pb(II) diethyl-DTC dibutyl-DTC; 6 = Pb(II) diethyl-DTC dipropyl-DTC; 7 = Pb(II) bisdiethyl-DTC.

Reaction 1 does not take place between bisdialkyl-DTC complexes of copper (I) or cobalt (II).

Another interesting feature is the ligand exchange between the bisdialkyl-DTC

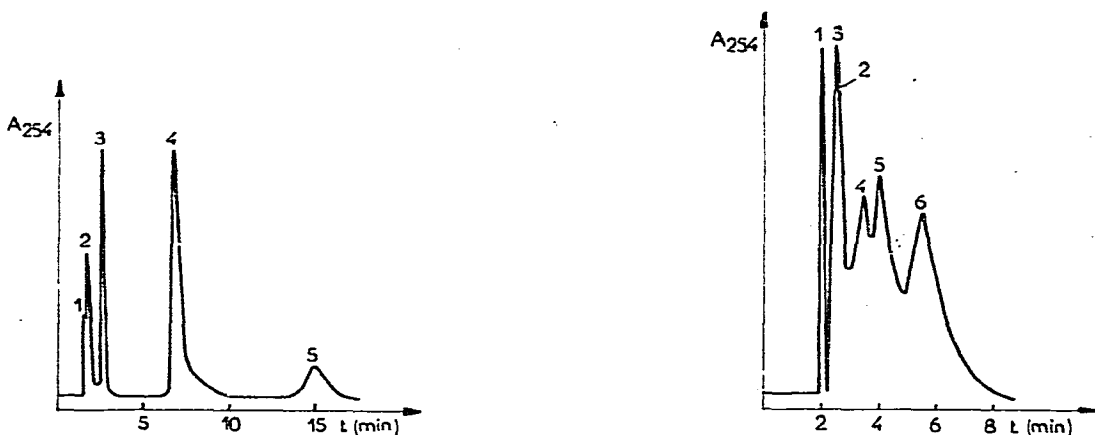
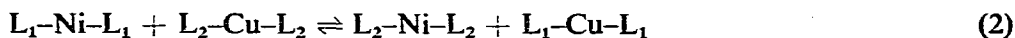


Fig. 7. Separation of Co(II) bisdialkyl-DTC complexes. Solvent: 40% dichloromethane in carbon tetrachloride; inlet pressure, 9.81 MPa; solvent velocity,  $0.26 \text{ cm} \cdot \text{sec}^{-1}$ ; other conditions as in Fig. 5. Peaks: 1 = inert; 2 = Co(II) bisdibutyl-DTC; 3 = Co(II) bisdipropyl-DTC; 4 = Co(II) bisdiethyl-DTC; 5 = Co(II) bisdimethyl-DTC.

Fig. 8. Analysis of a mixture of Cu(II) bisdiethyl-DTC and Ni(II) bisdibutyl DTC complexes. Solvent: 30% v/v dichloromethane in carbon tetrachloride. Inlet pressure, 4.22 MPa; solvent velocity,  $0.21 \text{ cm} \cdot \text{sec}^{-1}$ ; other conditions as in Fig. 5. Peaks: 1 = inert; 2 = Cu(II) bisdibutyl-DTC; 3 = Ni(II) bisdibutyl-DTC; 4 = mixed-ligand complex Ni(II) diethyl-DTC dibutyl-DTC; 5 = Cu(II) bisdiethyl-DTC; 6 = Ni(II) bisdiethyl-DTC.

complexes of different metals. The reaction does not lead to the unsymmetrical complexes, as might be expected, but as illustrated by Fig. 8, total ligand exchange occurs according to the reaction



This reaction was also verified by nuclear magnetic resonance spectroscopy in pure chloroform<sup>4</sup> and by square-wave polarography of the eluate of the spots separated by thin-layer chromatography on a silica gel plate<sup>5</sup>. The newly formed complex  $L_2\text{-Ni-L}_2$ , however, reacts with the original  $L_1\text{-Ni-L}_1$  complex according to eqn.1. On the other hand, ligand exchange does not occur between copper(II) bisdialkyl-DTC complexes.

In conclusion, HPLC is a valuable method for the separation of mixtures of metal bisdialkyl-DTC complexes. The search for selective phase systems for other metal chelates containing different ligands will be continued. The analysis of these complexes in the environment is hindered by the ease with which the ligand-exchange reactions between many of them occur.

#### REFERENCES

- 1 O. Liška, G. Guiochon and H. Colin, *J. Chromatogr.*, 171 (1979) 145.
- 2 O. Liška, J. Lehotay, E. Brandšteterová and G. Guiochon, *J. Chromatogr.*, 171 (1979) 153.
- 3 G. D. Thorn and R. A. Ludwig, *The Dithiocarbamates and Related Compounds*, Elsevier, Amsterdam, New York, 1962.
- 4 E. Beinrohr, *Collect. Czech. Chem. Commun.*, in press.
- 5 J. Černák, unpublished results, 1976.