Deuteration of methanol slightly increases τ. The presence of the small solvent isotope effect suggests a small component of CTTS character in the luminescence transition.

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Complex Metal Hexachlorostannates with Organic Molecules with Nitrogen Atoms as Donors

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Using donicity [1–3] as a term to reflect the complexing properties of the substances in CCl_4 as solvent, a great number of metal hexachlorostannates could be obtained with different ligands of lower donicity as that of the water [4–6] and higher one [7].

The present paper contains data regarding the preparation of coordination compounds in CCl_4, as solvent, with $SnCl_4$ as chlorine acceptor in Li, Na, K, Rb and Cs as alkalichlorides whose cation has been put to react with organic compounds containing nitrogen donor atom, functioning as ligands that have complexed the metal cation. The general formula of the coordination compounds in solutions is $(ML)_2$-$SnCl_6$, where the ligand L could be trimethyl-amine, dimethyl-amine, n-butyl-amine, ethylene-diamine, tetramethylethylene-diamine, pyridine, 2-methylpyridine and quinoline.

As the reactions are strongly exothermic they have been carried out in 1*M*-solutions in CCl_4 referring to each reactant: $SnCl_4$ and the ligand L. The alkali chlorides have been added to the solution of $SnCl_4$ in CCl_4 after the solution of $SnCl_4$ in CCl_4, added slowly, had led to an abundant formation of stable complex precipitates, which have been filtered and washed with CCl_4.

It is interesting to note that an attempt to obtain complexes using CuCl showed that no analogous complexation is achieved and the reaction does not yield a unitary product, while a darkening of the solution to dark blue has been observed, explained through the formation of Cu(II) aminocomplexes.

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Structural-Energetical Aspects of Interreaction in Carbonyl Metal Systems

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Theoretical arguments have so far been based on the earlier unknown facts of the possibility of the tensimetric method with the membrane zero-manometer for the definition of the solubility and thermodynamic properties of the dissolution process. In this report the structures of metal carbonyls are compared with the thermodynamic characteristics of the dissolution process of the same compounds and clusters form of the group elements. The alternation of the characteristic frequencies of M–C and C–O bonds of iron carbonyls gives the possibility to consider that the negative end of dipole moment, the order bond and the dissociation energy of metal carbonyl bond (DM –CO) do not increase practically and remain constant with considerable investment of the energy of metal–metal bond in dodecacarbonyl. It means that three-bridged bonds in $Fe_2(CO)_9$ stabilize its molecule and weaken the metal–metal bond and therefore the molecule $Fe_2(CO)_9$ becomes less active. There is no such effect in $Fe(CO)_5$, the negative effect does not almost change, and the molecule is less active. The increasing of negative end of dipole moment, the order bond and the dissociation energy of metal-carbonyl bond in $Fe_3(CO)_{12}$ promote the displaying of M–M interaction with the molecules of the dissolvents $Ni(CO)_4$ and $Fe(CO)_5$ and it increases solubility. The endothermical effect of dissolution of $Fe_3(CO)_{12}$ in $Fe(CO)_5$ in comparison with its dissolution in $Ni(CO)_4$ shows more stable interaction with $Fe_3(CO)_{12}$. The increased solubility of $Fe_3(CO)_{12}$ in $Fe(CO)_5$ in comparison with $Fe_2(CO)_9$ is also due to the structural and energetic peculiarities.

The solubility of cobalt carbonyls is considerably increased on increasing the number of M–M bonds in a cluster. At the same time the reduction of the CO-groups decreases the negative dipole of the metal-carbonyl bond and increases the tendency to the metal–metal interaction for the steric factor is conductive to it. Therefore, the forces of cross-interaction become more stable than the forces of interaction between homogeneous molecules and the dissolution process is less endothermic. Thermodynamic data of dissolution exhibit a particular role in the M–M bond in a cluster compound and in the formation of more stable complexes (associate) in the solution with other carbonyls.

The general role for dissolution processes of the compounds with a symmetrical structure is to increase the endotherm with substitution of $Ni(CO)_4$ with $Fe(CO)_5$. This regularity is due to the influence of filling and increasing of dissociation energy of dymetric molecules of nickel tetracarbonyl and iron pentacarbonyl. The exothermic effect of interaction of $M_2(CO)_{10}$ with $Ni(CO)_4$ leads to the advantage of energy as a result of smaller loss of energy with isolation of a molecule from the crystal and therefore $Mn_2(CO)_{10}$ is a more active compound and its solubility is in a great extent higher than that of $Re_2(CO)_{10}$.

Enhancement of Axial Coordination by β-Substitutions on Ni^{II}TPP

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The coordination ability of solvent molecules in metalloporphyrins is directly dependent on the nature of the central metal ion and on its valency. Because of the conjugated nature of the porphyrin ring system, electron donating or withdrawing substituents on the periphery of the molecule have been shown to affect the basicity of the porphyrin nitrogens [1, 2]. This, in turn, often affects the visible absorption spectra, redox potentials and axial ligation reactions of metalloporphyrins complexes [3–6]. Earlier spectrometric measurements on Ni(II) unsubstituted and *para*-substituted porphyrins showed the weak complexation of Ni(II) with strong Lewis bases [3].

Using electrochemical measurements on NiTPP (*1*) and NiTPP $(CN)_4$ (*2*) we demonstrate that the influence of β-substituted cyano-groups is particularly striking when compared to the very weak (on quasi-absence) interaction of Ni(II) with Lewis bases, in the unsubstituted porphyrin.

In DMF, the potential $E_{1/2}$ shifts (for the first reduction step of *2*), with increasing pyridine concentration, and reveals the formation of $NiTPP(CN)_4(Py)_n$ complexes (*3*), according to the following equilibria:

$$NiTPP(CN)_4 + Py \rightleftarrows NiTPP(CN)_4(Py) \qquad (K_1)$$

$$NiTPP(CN)_4(Py) + Py \rightleftarrows NiTPP(CN)_4(Py)_2 \qquad (K_2)$$

The very similar values of K_1 and K_2 were determined by using the relation of Kuta [7]:

$$F_o(L) = -RT/nF \sum_j k_j\{L\}^j = \exp(-nF/RT\ \Delta E_{1/2})$$

If water, instead of Py, is added, nickel in *2* forms only the monoliganded complex $Ni(TPP(CN)_4(H_2O)$ (*4*). In the same experimental conditions the redox potential of *1* does not shift significantly with neither pyridine nor water. These results agree with independent spectrometric measurements [6] carried out with pyridine in chloroform solution.

On kinetic point of view, a slow down is observed for the heterogeneous electrochemical rate constants of the electron transfer rate corresponding to the order of the calculated values for the equilibrium constants.

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