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]:

$$F_0(L) = -\,RT/nF \sum_j k_j\{L\}^j = \exp(-nF/RT\ \Delta E_{1/2})$$

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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Solvent Effects on VIb Metal Carbonyls Oxidation and Reduction Potentials

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The electrochemical behaviour of $M(CO)_6$, $\{M_2(CO)_{10}\}^{2-}$, $\{M_2H(CO)_{10}\}^-$ and $M(CO)_5S$ (M = Cr, Mo, W) has been studied [1] on mercury or platinum electrodes in several solvents S (acetonitrile, AN; propylene carbonate, PC; Acetone, A; N,N-dimethylformamide, DMF and dimethylsulfoxide, DMSO) characterized by a wide range of donor numbers [2]. The experimental study has been focused on the following main factors:

i) In a given solvent, the effect of the metal on the reduction potentials ($E^{cath}_{1/2}$), from $Cr(CO)_6$ to $W(CO)_6$.

ii) For each of the three $M(CO)_6$ complexes, the solvent effects on $E^{cath}_{1/2}$.

iii) For a given metal carbonyl, in a given solvent, the effect on $E^{cath}_{1/2}$ of substituting the ligand CO by solvent molecule(s).

The main results are the following:

1) In a given solvent, changing the metal M in $M(CO)_6$ induces a positive shift of $E^{cath}_{1/2}$, from $Cr(CO)_6$ to $W(CO)_6$, all other parameters being held constant. Also, the first monoelectronic oxidation of $M(CO)_6$ requires increasing energy from $Cr(CO)_6$ to $W(CO)_6$. These results may qualitatively be ascribed to an increasing metal to ligand π back-donation, from $Cr(CO)_6$ to $W(CO)_6$.

2) For a given metal M, the reduction of $M(CO)_6$ is facilitated as the donor number DN of the solvent increases. On the contrary, the reduction potential does not parallel the acceptor number AN of the solvent.

3) Gradual substitution of CO by CH_3CN in $W(CO)_6$ facilitates the oxidation and makes the reduction more difficult (except for $W(CO)_5(CH_3CN)$). This is fully consistent with the fact that CH_3CN is a weaker π acceptor than CO.

In conclusion, it is possible to rationalize these effects in terms of metal-to-carbon π back-bonding whose reinforcement results in a facilitated reduction and in a hindered oxidation, from $Cr(CO)_6$ to $W(CO)_6$. Also, the influence of the donor number of the solvent upon the $E^{cath}_{1/2}$ supports the reduction scheme previously proposed [1] for $M(CO)_6$, where the stable species, $M(CO)_5S$, results from the coordination of $M(CO)_5^-$ to the solvent S. In such a reaction indeed, a strengthened coordination of S on the metal is expected as DN of S increases, the consequence of which is to facilitate the reduction process, as observed experimentally.

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Complexes of Bipositive Metal Ions from Vanadium(II) to Copper(II) with Tris(3,5-dimethyl-1-pyrazolylethyl)amine

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Metal complexes of polypyrazolyl ligands have been found to provide significant examples of bioinorganic models [1]. As a part of a general investigation on this class of complexes [2], the study of compounds of the bipositive ions from vanadium(II) to copper(II) with the potentially tetradentate ligand tris(3,5-dimethyl-1-pyrazolylethyl)amine(TPy-EA) has been undertaken.