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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(TPyEA) has been undertaken.

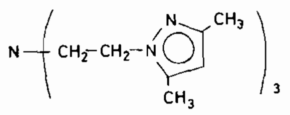

TABLE I. Some Representative Complexes of the Ligand TPyEA.

	μ_{eff} μ_B	Coordination Geometry
{$V(NCS)_2$(TPyEA)}	3.81	octahedral
[CrBr(TPyEA)] $BPh_4 \cdot C_2H_5OH$	4.83	trig. bipy ⟷ square pyr.
[MnBr(TPyEA)] $BPh_4 \cdot 0.5CH_2Cl_2$	5.86	trigonal bipyramidal
[FeCl(TPyEA)] $BPh_4 \cdot 0.5CH_2Cl_2$	5.50	trigonal bipyramidal
[Co(NCS)(TPyEA)] BPh_4	4.43	trigonal bipyramidal
[Co(TPyEA)] $(BPh_4)_2$	4.22	trigonal pyramidal
[Co(TPyEA)] $CoBr_4$	4.48	trig. pyr. + tetrahed.
[NiBr(TPyEA)] BPh4	3.26	trigonal bipyramidal
[$Cu(ClO_4)$(TPyEA)] ClO_4	1.88	trig. bipy. ⟷ square pyr.

The formulae of some representative complexes are reported in Table I. The assignment of the coordination geometry (Table I) is straightforward for the complexes of vanadium(II), manganese(II), iron(II), and nickel(II) on the basis of their physicochemical properties. The chromium(II) and copper(II) complexes, which are five-coordinate, presumably possess geometries intermediate between a trigonal bipyramid and a square pyramid.

Cobalt(II) complexes with different stoichiometries have been obtained depending on the starting materials and experimental procedures. The complexes with formulae [Co(TPyEA)] Y_2 (Y = BPh_4, BF_4, ClO_4) and [Co(TPyEA)] [MX_4] (M = Co, X = Br, I; M = Zn, X = Br) possess some unusual properties. As the ligand is potentially tetradentate, the coordination number of cobalt(II) cannot be more than four. However the electronic spectra of solid complexes as well as of the acetone and methanol solutions are typical of five-coordinate trigonal bipyramidal complexes of high-spin cobalt(II) [3] and are close to the spectrum of the five-coordinate [Co(NCS)(TPyEA)] BPh_4 derivative. A trigonal pyramidal geometry is tentatively assumed for the $[Co(TPyEA)]^{2+}$ cation in which the apical nitrogen atom averages the donor strength of two donors in an axially elongated trigonal bipyramidal geometry.

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Interaction of Dicobaltoctacarbonyl with Some Organic Solvents

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$Co_2(CO)_8$ is known to have different chemical behaviour when it is dissolved in common organic solvents, according to their properties.

Hydrocarbon solvents do not react with the solute: anyway, an equilibrium is established between at least three isomeric forms of $Co_2(CO)_8$, one with bridging COs (the only form present in solid state), the others with all COs terminal [1].

Solution in solvents which are hard Lewis bases, B, gives rise to a disproportionation reaction [2], whose general stoichiometry is:

$$3\,Co_2(CO)_8 + 12\,B \rightarrow 2[CoB_6^{++}]\,[Co(CO)_4^-]_2 + 8CO$$

The kinetic behaviour is very complicated and suggests the presence of several competing mechanisms, involving CO dissociation, base coordination and electron transfer [3]. The reaction rates are sensitive more to the steric characteristic of the base than to its basicity or to its dielectrinc constant.

When $Co_2(CO)_8$ is dissolved in CS_2 at room temperature, it reacts slowly with the solvent to yield a great variety of C–, S– or C_xS_y– containing cobalt carbonyl derivatives [4].

The most part of them shows structures in which a particular stable pyramidal unit Co_3E (E = C or S) is present. The pyramids are linked by metal–metal bond or by groups (or atoms) formed from CS_2 or by