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ELECTROCHEMISTRY OF TRANSITION METAL CLUSTERS

PAUL LEMOINE

Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide, E.R.A. au C.N.R.S. no. 468, Université Louis Pasteur - Institut Le Bel, 4, rue Blaise Pascal, 67000 Strasbourg (France)

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CONTENTS

A. INTRODUCTION

Considerable interest has been aroused in recent years concerning the role of transition metal clusters as: (i) homogeneous catalysts [1–4] and pre-

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cursors of new heterogeneous catalysts; (ii) model compounds for metal surfaces [5–8]; (iii) reactive sites of natural enzymes for hydrogen metabolism (hydrogenase and nitrogenase) and models of biological systems [9–12]. Hence, the synthesis and reactivity of transition metal clusters have been extensively studied [13]. According to Cotton and Wilkinson [14] "a metal atom cluster may be defined as a group of two or more metal atoms in which there are substantial and direct bonds between the metal atoms". A more limited definition also exists [15]: "a cluster is a molecule in which each metallic atom is directly bonded to at least two other metallic atoms", the simplest compound thus being triangular M_3L_n ($M =$ metal, $L =$ ligand). The term "cluster" is often indiscriminately used when there is no direct metal–metal bond in a coordination compound. In general, a cluster consists of a metallic framework surrounded by ligands. The metallic chain may be either open or closed within the more general definition [14]. Distinctions are also made between homometallic and mixed-metal clusters.

These polymetallic compounds are expected to have several advantages over monometallic systems, i.e.: (i) the ability to undergo multielectron transfer processes and thus to act as an "electron reservoir" or, in extreme cases, as an "electron sponge"; (ii) the ability to activate via metal–ligand bonds small molecules such as CO, N_2, CO_2, H_2, and olefins; (iii) the potential to electrochemically break metal–metal bonds thus yielding reactive sites on certain metal atoms, which facilitate the coordination of incoming molecules; (iv) selective activation of certain substrates (e.g. the FeMo system in nitrogenase) when the cluster involves more than one type of metal; (v) the potential to decompose after adsorption on a catalytic support yielding small metal crystallites.

The homogeneous catalysts typically involved in hydroformylation, hydrogenation or oligomerisation are monometallic complexes [3]. Since only one metallic atom acts as the active site in these catalysts, it is not surprising that clusters with a variety of metallic sites and geometries show unique and specific reactivity. It is therefore important to explore the redox behaviour of these metal–metal bonded complexes called "clusters". An earlier review [16] of the electrochemistry of transition metal organometallic compounds included only a brief mention of the redox behavior of clusters together with other carbonyl metal and metal–metal bonded organometallic complexes. Since then, numerous reports have appeared on the redox properties of clusters and it now seems appropriate to present a systematic review of the results obtained in this rapidly expanding field.

Section C is devoted to the early electrochemical studies of clusters and trimetallic linear complexes. Section D is concerned with reversible oxidation states in clusters, the most important aspect of this paper. Section E summarizes the paramagnetic cluster species studied by ESR spectroscopy.

TABLE 1

Physical properties and maximum potential range of several common solvents used for cluster electrochemistry

Solvent	Gutmann donicity [17]	F.p. (°C)	μ_D	B.p. (°C)	Cathodic limit [a]		Anodic limit [a]	
					Pt	Hg	Pt	Hg
Methylene chloride (CH_2Cl_2)	-	−96.7	1.5	40	−1.9	−1.9	+1.8	0.6
Acetonitrile (AN)	14.1	−45.7	3.92	81.6	−2.0	−2.8	+1.8	+0.6
Tetrahydrofuran (THF)	20.0	−108.5	1.7	65	−3.6	−3.6	+1.8	0.0
Dimethylformamide (DMF)	26.6	−61	3.86	153	−2.5	−3.0	+1.6	+0.5
Dimethyl sulfoxide (DMSO)	29.8	18.5	3.96	189.0	−1.9	−3.0	+0.7	+0.4
Propylene carbonate (PC)	15.1	−48.8	4.98	241.7	−2.0	−3.0	+1.6	+0.6

[a] Values given are the maximum limits observed in the literature and are reported vs. SCE. These values may be substantially less depending on the type of supporting electrolyte and the purity of the solvent.

This is followed by data on metal–halide clusters and metal tetrathiolene clusters in Section F. Finally, applied aspects of the electrochemistry of clusters, such as biological and charge-transfer applications, will be reviewed in Section G.

B. EXPERIMENTAL CONDITIONS FOR ELECTROCHEMICAL STUDIES OF CLUSTERS

Since most clusters are insoluble in water (except the metal–halide complexes), a variety of organic solvents has been used, the most common being CH_2Cl_2, CH_3CN, CH_3COCH_3, DMF, 1,2-dimethoxyethane, propylene carbonate, THF and DMSO, the donor numbers (DN) of which are given by Gutmann [17]. The supporting electrolytes used in non-aqueous media are generally quaternary ammonium salts such as TEAP (tetraethylammonium perchlorate), TBAP (tetra-n-butylammonium perchlorate) and TBHP (tetra-n-butylammonium hexafluorophosphate).

The physical and electrochemical characteristics (Table 1) of the solvents used have been described in numerous reports [18–20]. The working electrodes are frequently solids such as platinum or gold for which the available anodic potential range is wide compared to that of the mercury electrode. The dropping mercury electrode or the hanging mercury drop electrode have also been used for electroreduction purposes for which a Pt electrode is equally viable. The reference electrode is often the saturated calomel electrode (SCE) or the Ag/Ag^+ electrode. Most studies have employed cyclic voltammetry in association with controlled potential coulometry. The products obtained by coulometry have occasionally been compared with those obtained by chemical reduction or oxidation (e.g. with NaHg and $NaBH_4$ or NO^+ and Ag^+). Attempts have been made to isolate and characterize the reduction or oxidation products.

Some authors have used polarography or stationary voltammetry on a rotating disc electrode in order to obtain potentials. Low-temperature electrochemistry is often necessary for stabilizing the electrochemically generated species. In situ ESR coulometry permits detection of paramagnetic species during redox reactions. The original references [21–27] should be consulted for details of the experimental conditions in each case.

C. EARLY STUDIES ON CLUSTERS AND METAL–METAL BONDED COMPLEXES

(i) *Electrochemical reduction of $M_3(CO)_{12}$ (M = Fe, Ru, Os)*

According to Vlcek [28,29], $Fe_3(CO)_{12}$ (Fig. 1) is reduced in two steps at a dropping mercury electrode leading probably to $[Fe_3(CO)_{12}]^{2-}$. This anion gives an anodic wave with almost the same $E_{1/2}$ as that of the first reduction wave of $Fe_3(CO)_{12}$. Later, Dessy et al. [30] obtained more cathodic reduction waves for the same complex, probably due to the decomposition of the cluster in the polar solvent.

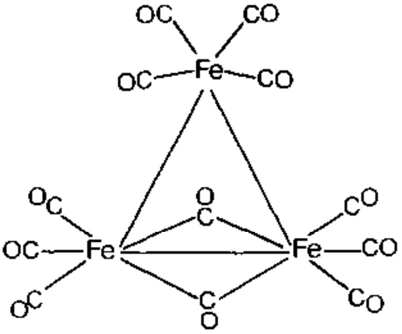


Fig. 1. The $Fe_3(CO)_{12}$ cluster.

Further studies [32] on $Fe_3(CO)_{12-n}L_n$ [$n = 0$–3, $L = PPh_3$, $P(OMe)_3$, $P(OPh)_3$] showed two well defined reduction waves in freshly prepared solutions ($E_{1/2} = -0.21$ and -0.76 V vs. Ag/Ag^+ in CH_3COCH_3). The first reduction step was reversible at a platinum electrode at 268 K and was assigned to the formation of a radical anion

$$Fe_3(CO)_{12} + e^- \rightleftharpoons [Fe_3(CO)_{12}]^{\cdot -}$$

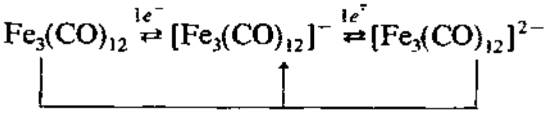
The ESR spectrum of this anion was obtained [31]. Substitution of a phosphine ligand for one of the CO ligands resulted in a negative shift of the first reduction wave as predicted by the increased charge on the iron atoms; this substitution also accelerates the decomposition of the radical anion.

The addition of a second electron to $Fe_3(CO)_{12}$ is described as

$$[Fe_3(CO)_{12}]^{\cdot -} + e^- \rightarrow [Fe_3(CO)_{12}]^{2-} \xrightarrow{\text{(chem)}} \text{products}$$

at more negative potentials. Fragmentation of the cluster was suggested and this reduction process was found to be irreversible.

Recent work by Vlcek and co-workers [33] confirms these earlier results. In CH_2Cl_2 and TBHP, $Fe_3(CO)_{12}$ undergoes two one-electron reductions ($E_{1/2} = -0.44$ and -0.83 V vs. SCE). The first step is reversible and leads to the paramagnetic species $[Fe_3(CO)_{12}]^{\cdot -}$ which decomposes in a complicated manner. The second step is not fully reversible ($\alpha = 0.83$) and generates $[Fe_3(CO)_{12}]^{2-}$ which reacts rapidly with the neutral cluster to give $[Fe_3(CO)_{12}]^{\cdot -}$. The following reduction scheme is given by Vlcek and co-workers [33]



$$Fe_3(CO)_{12} \overset{1e^-}{\rightleftharpoons} [Fe_3(CO)_{12}]^- \overset{1e^-}{\rightleftharpoons} [Fe_3(CO)_{12}]^{2-}$$

Comparison of the electrochemical behaviour of $Fe_3(CO)_{12}$ with that of its analogs $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ was reported by Bond et al. [32]. $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ both show two reduction steps. The first step is both chemically and electrochemically irreversible even at 195 K. The $E_{1/2}$ values are more negative than that of $Fe_3(CO)_{12}$ and have been reported as -0.88 V for $Ru_3(CO)_{12}$ and -1.16 V for $Os_3(CO)_{12}$. The following scheme has been proposed (M = Ru, Os)

$$M_3(CO)_{12} + e^- \rightarrow [M_3(CO)_{12}]^{\cdot -} \rightarrow \text{products}$$

The second ill defined wave is probably due to an electrode process involving a fragmentation product of the clusters.

(ii) Other clusters and polymetallic complexes

Dessy et al. [30,34] have examined the cathodic behaviour of more than 100 organometallic complexes in 1,2-dimethoxyethane (DME) containing 0.1 M TBAP at a mercury electrode (vs. Ag/Ag^+ 10^{-3} M reference electrode). Some of the clusters and polymetallic complexes are listed in Table 2. Systems 1–6 all exhibit a one-electron electrochemically reversible reduction. The case of $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$ (system 2) will be discussed separately below. After exhaustive reduction, reoxidation of the electrochemically generated anions gave back the starting material, except for system 5. The species $[(\eta^5\text{-}C_5H_5)Co(CO)]_3$ shows two electrochemically reversible steps. The first four clusters (1–4) have a chemistry similar to that of the metallocenes and therefore their reversible reduction is not surprising. System 6 is an acetylene–metal carbonyl complex.

The polymetallic compounds listed in Table 2 have been divided by Dessy et al. [34] into three categories. (a) Systems 10–13 are linear trimetallic species with a metallic core m–Hg–m (m denotes a carbonyl metallate moiety). They each undergo a two-electron reduction yielding mercury and two carbonyl metallate anions according to

$$\text{m–Hg–m} + 2e^- \rightarrow Hg + 2m^- \; (m = Mn(CO)_5,$$
$$Cr(CO)_3(\eta^5\text{-}C_5H_5),\; Mo(CO)_3(\eta^5\text{-}C_5H_5))$$

(b) Systems 7 and 8 exhibit a two-electron reduction resulting in the rupture of the metal–metal bond. System 9 is not well understood but seems to

TABLE 2

Some results of Dessy et al. [30,34] on the reduction of organometallic complexes

System	Formula	$-E_{1/2}$	n	Reduction products [a]
(a) Clusters				
1	$[\eta^5\text{-}C_5H_5Mo(CO)PPh_2]_3$	2		Stable redn. species
2	$[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$	1.9	cycles	
3	$[(\eta^5\text{-}C_5H_5)Co(CO)]_3$	1.6	1	Stable anion
4	$(\eta^5\text{-}C_5H_5)_3Ni_3(CO)_2$	1.5	1	Stable anion
5	$Fe_3(CO)_{12}$	1.6 2.4	1	Not $[HFe_3(CO)_{11}]^-$
6	$Fe_3(CO)_8(PhC_2Ph)_2$ two structural isomers	1.56 or 1.3	1	Radical anion
(b) Polymetallics				
7	$(\eta^5\text{-}C_5H_5)Mo(CO)_3\text{-}SnMe_2\text{-}Mo(CO)_3(\eta^5\text{-}C_5H_5)$	1.8	2	2 Mo: + Me_2Sn
8	$(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{-}SnMe_2\text{-}Fe(CO)_2(\eta^5\text{-}C_5H_5)$	2.7	2	2 Fe:$^-$ + Me_2Sn
9	$[(\eta^5\text{-}C_5H_5)Mo(CO)_3]_2Sn[Fe(CO)_2(\eta\text{-}C_5H_5)]_2$	1.8 2.0 2.5		
10	$[\eta^5\text{-}C_5H_5Cr(CO)_3]_2Hg$	1.3	2	2 Cr:$^-$ + Hg
11	$[\eta^5\text{-}C_5H_5Mo(CO)_3]_2Hg$	1.3	2	2 Mo:$^-$ + Hg
12	$[(OC)_5Mn]_2Hg$	1.1	2	2 Mn:$^-$ + Hg
13	$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2Hg$	2.0	2	2 Fe:$^-$ + Hg
14	$Ph_3Sn\text{-}Se\text{-}SnPh_3$	2.4	1	Ph_3SnSe^-: + Sn^-
15	$Ph_3Sn\text{-}Se\text{-}GePh_3$	2.4	1	Ph_3SnSe^-: + GeH

[a] Mn = $Mn(CO)_5$, Fe = $(\eta\text{-}C_5H_5)Fe(CO)_2$ etc.

involve the electrochemical fragmentation of organometallic side chains at each reduction step. (c) Systems 14 and 15 undergo unsymmetrical cleavage of one metal–metal bond after the first one-electron reduction.

In general, electrochemical reduction of these metallic chain compounds results in the rupture of one or two metal–metal bonds: the electrochemical (and chemical) reduction is therefore irreversible. The LUMO involved in reduction is in most cases an antibonding orbital of metal character. Similar behaviour has been observed in other metallic chain complexes [35,36].

(iii) Linear trimetallic complexes

These complexes are analogous to those (10–13) described in Table 2. The linear trimetallic $(CO)_4Co{-}Hg{-}Co(CO)_4$ was first studied by Vlcek [37]. Electrochemical reduction was undertaken at a dropping mercury electrode and the following reduction scheme was proposed

$$(CO)_4Co{-}Hg{-}Co(CO)_4 + 2e^- \rightleftharpoons Hg + 2\ Co(CO)_4^-$$

This result was later confirmed by the Montauzon [38]. The value of $E_{1/2} = -0.96$ V vs. Ag/Ag^+ 0.1 M was obtained in THF with 0.1 M TBAP on a mercury electrode.

Denisovich et al. [39,40] studied other trimetallic complexes. The species $Hg[(\eta\text{-}C_5H_5)W(CO)_3]_2$ was reduced on a mercury electrode at $E_{1/2} = -0.77$ V vs. SCE in CH_3CN according to

$$Hg[(\eta^5\text{-}C_5H_5)W(CO)_3]_2 + 2e^- \rightarrow 2[(\eta^5\text{-}C_5H_5)W(CO)_3]^- + Hg$$

The same two-electron reduction occurs for the manganese analog at $E_{1/2} = -0.74$ V vs. SCE

$$Hg[Mn(CO)_5]_2 + 2e^- \rightarrow 2[Mn(CO)_5]^- + Hg$$

The trimetallic linear complexes $Hg[Co(CO)_3L]_2$ and $HgCo_2(CO)_{8-n}L_n$ [$L = PR_3$, $P(OR)_3$] have also been studied at a mercury electrode [41]. The $E_{1/2}$ values are dependent on L and n and are related to the basicity of the ligand L as well as to the CO stretching frequencies of the molecules. The reduction scheme is

$$Hg[Co(CO)_3L]_2 + 2e^- \rightarrow Hg + 2[Co(CO)_3L]^-$$

A comparative study of the electroreduction of the linear trimetallic complexes M–Hg–M, $(M{-}Au{-}M)^-$ and $M{-}PtL_2{-}M$ where $M = Co(CO)_4$, $Cr(CO)_3(\eta^5\text{-}C_5H_5)$, $Mo(CO)_3(\eta^5\text{-}C_5H_5)$, $W(CO)_3(\eta^5\text{-}C_5H_5)$, $Mn(CO)_5$, $Fe(CO)_3(NO)$ and $L = Bu^tNC$ or cyclo-$C_6H_{11}NC$ was carried out at solid electrodes [35,36]. The following reduction scheme was suggested

$$\mathrm{M{-}Hg{-}M + 2e^- \rightarrow 2M^- + Hg}$$

$$\mathrm{(M{-}Au^I{-}M)^- + e^- \rightarrow 2M^- + Au}$$

$$\mathrm{M{-}Pt^{II}L_2{-}M + e^- \rightarrow M^- + M{-}Pt^IL_2}.$$

The unexpected $\mathrm{Pt^I}$ complexes were detected by ESR spectroscopy during

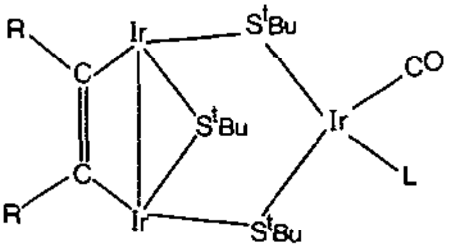


Fig. 2. The complexes studied by Lemoine at al. [42]: L=CO, R=CF_3 complex I; L=CO, R=COOMe complex II; R=CF_3, L=C_4F_6 complex III; R=CF_3, L=$POMe_3$ complex IV.

exhaustive electrolysis. Ligand-bridged polymetallic complexes were also studied. Thus, four trimetallic Ir complexes (I–IV, Fig. 2) were studied in CH_3CN containing 0.1 M TEAP at a platinum electrode [42]. These complexes undergo an irreversible one-electron reduction near $E_{1/2} = -1.3$ V vs. SCE leading to their destruction, although complex III is easier to reduce ($E_{1/2} = -1.1$ V) than the others in the medium used. They also show an irreversible one-electron oxidation near +1.3 V vs. SCE.

Electrochemical synthesis of linear trimetallic complexes has also been achieved [43]. The electrochemical oxidation of a Zn, Cd or In electrode was performed in the presence of $Co_2(CO)_8$ or $Mn_2(CO)_{10}$ in an organic solvent mixture containing a neutral bidentate donor ligand such as bipy. The heteronuclear complexes $M[M'(CO)_n]_m$ (M = Zn, Cd, In; M′ = Co, Mn; $n = 4,5$; $m = 2,3$) were thus obtained. Advantages of the synthesis were discussed and a mechanism for the process proposed.

To summarize, therefore, for an open metallic chain, the net result of electrochemical reduction is the rupture of at least one metal–metal bond: an antibonding orbital of metal–metal character being the site of electron gain. This reduction is almost irreversible, whereas for closed metallic chains it is often reversible and monoelectronic without destruction of the metallic framework.

D. REVERSIBLE ELECTROCHEMICAL GENERATION OF DIFFERENT OXIDATION STATES IN CLUSTERS

The majority of clusters reversibly change oxidation states, and are often termed “electron-reservoir” compounds. The case of $Fe_3(CO)_{12}$ and its Ru and Os analogs [31] was discussed in the preceding chapter.

(i) Redox behaviour of the Fe_4 framework cluster

Another interesting compound which has been studied electrochemically is the cluster $[Fe(CO)(\eta^5\text{-}C_5H_5)]_4$ [44] which is related to a series of homologous clusters in which the CO ligand is replaced by S. The species $[(\eta^5\text{-}C_5H_5)FeS]_4$ and $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$ have similar cristallographic structures, the Fe atoms being arranged in a tetrahedron which forms the metallic framework. Each $\eta^5\text{-}C_5H_5$ ligand is bonded to an iron atom and each CO or S ligand is triply bonded to three distinct iron atoms (Fig. 3). Initial studies of these species by Ferguson and Meyer [45] indicate that the cluster system remains intact in the five oxidation states +3, +2, +1, 0, −1 for $[(\eta^5\text{-}C_5H_5)FeS]_4$ (I) and in the four oxidation states +2, +1, 0, −1 for $[(\eta^5\text{-}C_5H_5)Fe(CO)]_4$ (II). In 0.1 M TBHP CH_3CN solutions, the $E_{1/2}$ values measured at a Pt electrode vs. SCE are

$$(\mathrm{I})^{3+} \overset{1.41\ \mathrm{V}}{\rightleftarrows} (\mathrm{I})^{2+} \overset{0.88\ \mathrm{V}}{\rightleftarrows} (\mathrm{I})^{+} \overset{0.33\ \mathrm{V}}{\rightleftarrows} \mathrm{I}^{-} \overset{0.33\ \mathrm{V}}{\rightleftarrows} (\mathrm{I})^{-}$$

$$(\mathrm{II})^{2+} \overset{1.07\ \mathrm{V}}{\rightleftarrows} (\mathrm{II})^{+} \overset{0.32\ \mathrm{V}}{\rightleftarrows} \mathrm{II}^{-} \overset{1.30\ \mathrm{V}}{\rightleftarrows} (\mathrm{II})^{-}$$

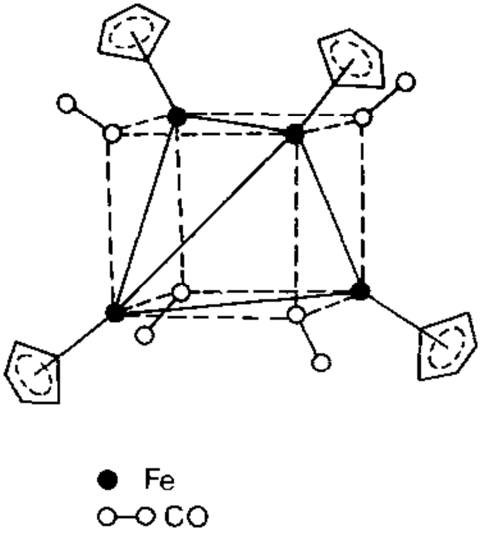


Fig. 3. The $[Fe(\eta^5\text{-}C_5H_5)L]_4$ cluster studied by Ferguson and Meyer [45].

An ESR signal due to the paramagnetic monocation $[(\eta^5\text{-}C_5H_5)FeS]_4^+$ was also obtained. Controlled potential electrolysis was used to prepare some of these ions in good yields. Solvent effects on the measured half-wave potentials for $[(\eta\text{-}C_5H_5)Fe(CO)]_4$ were determined; the $Fe_4^{+/0}$ couple is relatively insensitive to solvent change which suggests that this couple could be used as an electrochemical reference. The redox behavior of the various ions has been studied [46].

A study of the cluster $[Fe_4(\eta^5\text{-}C_5H_5)_4(\mu^3\text{-}S)_4]^n$ ($n = -1$ to $+3$) by Dahl and co-workers [47] was recently published. Mono- and di-cations were obtained by controlled potential electrolysis and isolated in the solid state. X-ray crystallographic analysis of the dication (with PF_6 as the counter-ion) reveals that the geometry of the Fe_4S_4 framework differs significantly from that in the neutral and monocationic homologs. Whereas the dicationic metallic core Fe_4S_4 shows two long and four short Fe–Fe distances (flattened tetrahedron), the neutral compound has two short (av. 2.64 Å) and four long (av. 3.36 Å) Fe–Fe distances and this elongated tetrahedron is twisted in the monocation such that several different Fe–Fe distances are observed. The monoanion and the trication have not yet been isolated but their probable structures may be predicted from structural studies on the neutral and dicationic species and from the unified qualitative MO cluster model. Electrochemical studies on $[Fe_4(\eta^5\text{-}C_5H_5)_4(\mu^3\text{-}S)_4][PF_6]_2$ indicate the existence of four reversible one-electron exchanges. Finally it was found that the Fe_4S_4 core in the Balch dianion [48] $[Fe_4\{S_2C_2(CF_3)_2\}_4(\mu^3\text{-}S)_4]^{2-}$ appears to be structurally and electronically similar to that of the dication $[Fe_4(\eta^5\text{-}C_5H_5)_4(\mu^3\text{-}S)_4]^{2+}$.

A homologous cluster of this series was previously synthesized and studied electrochemically [48]. Bernal et al. [49] established its structure. Polarographic measurements in CH_2Cl_2 of the dianion $[Fe_4\{S_2C_2(CF_3)_2\}_4(\mu^3\text{-}S)_4]^{2-}$ showed two anodic and two cathodic waves at nearly the same potentials as those obtained for the neutral cluster which exhibited four successive cathodic waves. Dahl and co-workers [47] have shown that during oxidation of the dianion to form the monoanion and the neutral cluster, electrons are removed from the dithiolene ligands instead of from the antibonding metal cluster orbitals, so that the metallic core remains unchanged. The compound $[AsPh_4]_2[Fe_4\{S_2C_2(CF_3)_2\}_4(\mu^3\text{-}S)_4]$ was isolated by Balch, but the -3 and -4 anions of the series could not be isolated, presumably because of their oxygen sensitivity.

Balch [48] also studied the series $[Fe_4(S_2C_2Ph_2)_4S_4]^n$ ($n = 0, -1$). The monoanion of $[AsPh_4]^+[Fe_4(S_2C_2Ph_2)_4S_4]^-$ was isolated and polarographic measurements of both it and the neutral complex showed that the former constituted the first reduced member of the series.

A series of synthetic analogs of the active sites of the iron–sulfur proteins

$[Fe_4S_4(SR)_4]^{2-,3-}$ have been examined polarographically [50] in Me_2SO/H_2O solutions containing buffered 0.1M $(Et_4N)BF_4$ [R = SEt, SCH_2CH_2OH, $SCH_2CH_2CO_2$, S-(RS)-Cys(Ac)NHMe, S-(S)Cys(Ac)NHMe, 12-peptide]. Their $E_{1/2}$ values are compared to that of an Fe_4 protein (Clostridium pasteurianum ferredoxin) and the differences, $\Delta E_{1/2}$, ascribed to the combined effects of protein structure and environment. Ferredoxins and related non-heme iron–sulfur proteins function as electron carriers in metabolic reactions. Some biological aspects of cluster electrochemistry will be discussed at the end of the present review (Section G).

Starting from $(Et_4N)_2[Fe_4S_4(SEt)_4]$ (I), a new cluster $(Et_4N)_2[Fe_4S_4(OPh)_4]$ (II), was obtained and isolated [51]. Species (II) is electrochemically reduced in two one-electron steps at potentials more cathodic than those of I. Phenoxide ligation makes the $Fe_4S_4^{2+}$ core more difficult to reduce. Thus, the normal Fe_4S_4 clusters with cysteine residue ligands will have similar or slightly more positive reduction potentials than $Fe_4S_4^{2+}$ centers coordinated to a protein via tyrosinate O-bonded residues.

(ii) A new redox series with nickel–cyclopentadienyl clusters

This topic has been the object of recent studies. The bipyramidal $Ni_6(\eta^5\text{-}C_5H_5)_6$ cluster was first synthesized by Paquette and Dahl [52]. Cyclic voltammetry of this complex (I) in CH_2Cl_2 containing 0.1 M TBHP on a gold electrode vs. SCE showed four one-electron reversible couples according to ($v = 500$ mV s^{-1})

$$(I)^{3+} \overset{+1\ V}{\rightleftarrows} (I)^{2+} \overset{+0.19\ V}{\rightleftarrows} (I)^{+} \overset{-0.26\ V}{\rightleftarrows} I \overset{-0.97\ V}{\rightleftarrows} (I)^{-}$$

The monocationic $[Ni_6(\eta^5\text{-}C_5H_5)_6]^+PF_6^-$ complex (II) exhibited five one-electron reversible couples with the following potential values obtained under the same experimental conditions but in CH_3CN as solvent

$$(II)^{2-} \underset{-1.74V}{\rightleftarrows} (II)^{-} \underset{-1.01\ V}{\rightleftarrows} (II) \underset{-0.42\ V}{\rightleftarrows} (II)^{+} \underset{+0.26\ V}{\rightleftarrows} (II)^{2+} \underset{+0.80\ V}{\rightleftarrows} (II)^{3+}$$

These preliminary results show that the Ni_6 cluster is "electron rich" in accordance with its structure.

The Fischer–Palm [53] $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu^3\text{-}CO)_2$ cluster first reduced by Dessy et al. [34] is a triangular Ni_3 cluster. It has been shown to contain an unpaired electron in an antibonding, in-plane, non-degenerate metallic orbital of the same type as the one containing the unpaired electron in $Co_3(CO)_9(\mu^3\text{-}S)$ [54]. Unfortunately, the efforts of Dahl and co-workers [55] to ascertain experimentally the antibonding nature of the HOMO failed: all attempts to

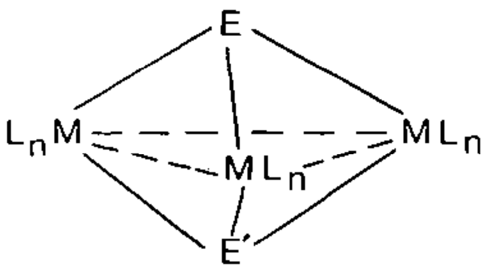


Fig. 4. The trimetallic clusters studied by Madach and Vahrenkamp [56]: E,E′ = S, CO, CS, SO; $ML_n = Fe(CO)_3$, $Ni(\eta^5\text{-}C_5H_5)$, $Co(\eta^5\text{-}C_5H_5)$ (see Table 3).

remove the unpaired electron of $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu^3\text{-}CO)_2$ by oxidation to the monocation were unsuccessful. However, recently Madach and Vahrenkamp [56] showed that the Fischer–Palm cluster may be oxidized irreversibly via a one-electron process.

(iii) Redox series in capped trinuclear clusters

In a recent study, Madach and Vahrenkamp [56] investigated trimetallic clusters of Fe, Co and Ni with triply bridging ligands such as S, CO, SO and CS (Fig. 4). As shown in Table 3, numerous oxidation states were obtained, classified according to the total number of valence electrons, *Z*, in the cluster. The reversible redox steps were differentiated from the irreversible steps, the number of which depended on the nature of the ligands E, E′ and on the number of electrons present in the cluster. The redox potentials were discussed according to the HOMO and LUMO levels. Similar studies were undertaken by the same authors on bimetallic V, Cr and Mn bridged complexes [57].

Another series of Co and Co–Fe triangular clusters showing reversible processes have been studied [58]. Clusters (1) and (2) are presented in Fig. 5. Electrochemically reversible processes were observed for the oxidation of (1) to $(1)^+$ and for the reduction of (2) to $(2)^-$. The authors assigned essentially bonding metal–metal interactions to the HOMO's in $(1)^+$ and (2). They concluded that the HOMO of (1) and the LUMO of (2) are almost exclusively combinations of metal *d* orbitals.

(iv) Redox properties of small metallocarborane clusters

Two triple-decker dicobalt species: 1,7,2,3-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ (I) and 1,7,2,4-$(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ (II) (Fig. 6) were studied on a Pt electrode in CH_2Cl_2 containing 0.1 M TBHP by Brennan and Geiger [59] and the results compared with those of monocobalt sandwiches such as 1,2,3-(η^5-

TABLE 3

The Fe, Co, Ni triangular clusters studied by Madach and Vahrenkamp [56] (see Fig. 4 for positions of L_nM, E, E′) [a]

L_nM	E	E′	Electrochemical step vs. the number of valence electrons, Z, present in the cluster							
			$Z=47$	$Z=48$	$Z=49$	$Z=50$	$Z=51$	$Z=52$	$Z=53$	$Z=54$
η^5-C_5H_5Ni	S	S		(+5)	←	+3	←	+1 ⇄	0 ⇄	−1
η^5-C_5H_5Co	S	S		+2 ⇄	+1 ⇄	0 ⇄	−1			
η^5-C_5H_5Ni	CO	CO	D←	+1 ⟵	0 ⇄	−1				
η^5-C_5H_5Co	S	CS	D←+1 ⟵	0 ⇄	−1					
$(CO)_3Fe$	S	CO	D←+1 ⟵	0 ⟶	−1					
$(CO)_3Fe$	S	S				0 ⇄	−1 ⟶	−2		
$(CO)_3Fe$	S	SO				0 ⟶	−1 ⟶	(−2)		

[a] D = destruction of the cluster.

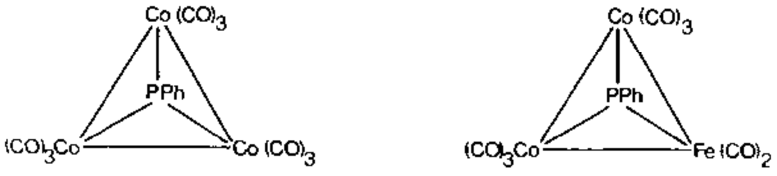


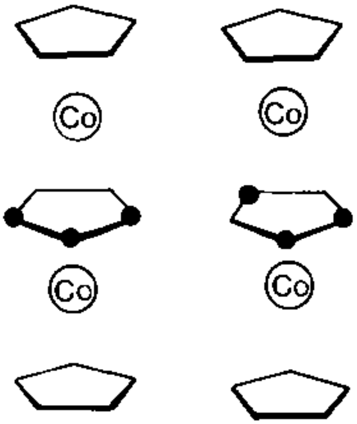
Fig. 5. Triangular clusters studied by Vahrenkamp and co-workers [58].

$C_5H_5)CoC_2B_4H_6$; 1,2,4-(η^5-$C_5H_5)CoC_2B_4H_6$; $(\eta^5\text{-}C_5H_5)_2Co^+$. Complexes (I) and (II) undergo a series of one-electron oxidations and reductions, each step being diffusion controlled and reversible. The general redox scheme is

$$\begin{array}{l} \\ \frac{\text{I:}}{\text{II:}} \end{array} \quad ? \leftarrow \left(\frac{\text{I}}{\text{II}}\right)^{2+} \underset{\frac{+1.72\text{ V}}{-}}{\rightleftarrows} \left(\frac{\text{I}}{\text{II}}\right)^{+1} \underset{\frac{+0.51\text{ V}}{+0.89\text{V}}}{\rightleftarrows} \underset{\frac{\text{I}}{\text{II}}}{(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5}$$

$$\underset{\frac{-1.44\text{ V}}{-1.35\text{ V}}}{\rightleftarrows} \left(\frac{\text{I}}{\text{II}}\right)^{-} \underset{\frac{-2.23\text{ V}}{-2.30\text{ V}}}{\rightleftarrows} \left(\frac{\text{I}}{\text{II}}\right)^{2-}$$

These results strongly support the assumption that the electronic structure is delocalized over the dianions, the negative charge being spread over both metals. Indeed, in the case of very weak electronic coupling, or strictly isolated cobalt reduction sites, a single two-electron wave or two closely spaced one-electron waves would be expected.



I II

Fig. 6. The complexes studied by Brennan and Geiger [59]. (● = BH); I = 1, 7, 2, 3-(η^5-$C_5H_5)Co_2C_2B_3H_5$; II = 1, 7, 2, 4-(η^5-$C_5H_5)Co_2C_2B_3H_5$.

(v) The surprising "electron-sponge" cluster

A trimeric ruthenium ligand-bridged cluster, $[(py)_2Ru_3O(OAc)_6(pyr)]_2[Ru_3O(OAc)_6(CO)]$ (py = pyridine, pyr = pyrazine, Ac = CH_3CO) synthesized by Meyer and co-workers [60] shows surprising redox properties: a series of ten one- or two-electron reversible waves were obtained by the authors who termed the complex an "electron sponge". Under the same experimental conditions, the isolated cluster units, $[Ru_3O(CH_3CO_2)_6(py)_2(pyr)]^+$ and $Ru_3O(CH_3CO_2)_6(CH_3OH)_2(CO)$, exhibit five oxidation states. As the electron number increases in oligomers containing a number of cluster sites, the electronic coupling between the cluster sites is enhanced. The appearance of a series of closely spaced one-electron waves may indicate the existence of a band-like behaviour and a metallic or semi-conductor-like intramolecular conductivity. In the isolated cluster unit, the interactions between the units are weak and therefore, since the total number of electrons is low, the redox properties are only those expected for isolated units [60]. This important contribution will hopefully lead electrochemists to study the redox properties of oligomeric clusters.

(vi) Redox behaviour of mixed transition metal clusters

In comparison with homogeneous clusters, mixed transition metal clusters should afford the advantages of multicentered selective activation for different molecules. This promising field has only recently been developed. Three triangular $CoNi_2$ metallic cores bridged by two CO ligands, surrounded by cyclopentadienyl ligands and substituted rings, were recently synthesized by Dahl and co-workers [61] (Fig. 7). Each of the three clusters, $(\eta^5\text{-}C_5H_{5-n}Me_n)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu_3\text{-}CO)_2$ ($n = 0, 1, 5$), exhibited a reversible one-electron $0/-1$ couple. In 1,2-dimethoxyethane and 0.1 M TBAP, on a Pt electrode the $E_{1/2}$ values are -1.525 V for $n = 0$, -1.558 V for $n = 1$ and

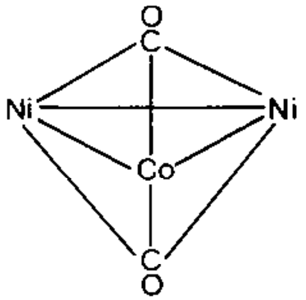


Fig. 7. The metallic core in the cluster studied by Dahl and co-workers [61].

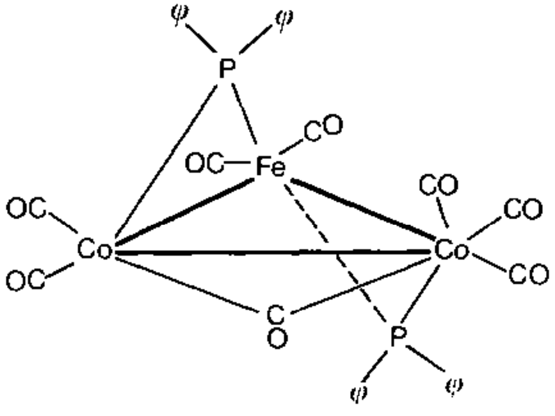
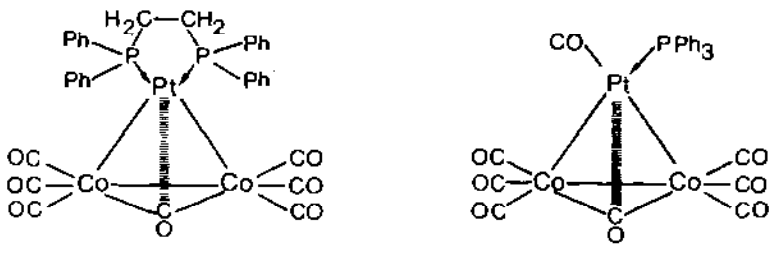


Fig. 8. The $FeCo_2$ cluster studied by Young [62].

-1.693 V for $n = 5$ (vs. Ag/Ag^+ reference electrode). An almost linear correlation between the $E_{1/2}$ values and the number (n) of methyl substituents on the cobalt coordinated $C_5H_{5-n}Me_n$ ring was obtained (a potential shift of -33 mV is observed between the $E_{1/2}$ values for $n = 0$ and $n = 1$). The monoanion $[(\eta^5\text{-}C_5Me_5)CoNi_2(\eta^5\text{-}C_5H_5)_2(\mu^3\text{-}CO)_2]^-$ has been isolated by exhaustive reduction of the neutral parent molecule.

These results should be compared with those obtained by Madach and Vahrenkamp [56] on the Fischer–Palm $Ni_3(\eta^5\text{-}C_5H_5)_3(\mu^3\text{-}CO)_2$ cluster, and on similar trimetallic compounds.

By reaction of $Fe(CO)_4(PPh_2PPh_2)$ with $Co_2(CO)_8$, Young [62] recently synthesized a triangular $FeCo_2(\mu\text{-}CO)(CO)_7(\mu\text{-}PPh_2)_2$ cluster (Fig. 8) which was studied electrochemically. Cyclic voltammetry of this novel compound showed three one-electron reduction waves at -1.01, -1.45 and -1.75 V vs. Ag/0.1 M Ag^+ in CH_3CN. The second wave appears reversible only at



I

II

Fig. 9. The $PtCo_2$ clusters studied by Lemoine et al. [63].

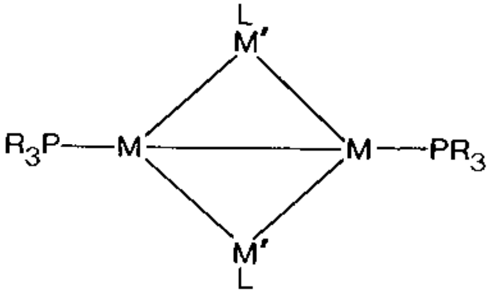


Fig. 10. The tetrametallic clusters studied by Jund et al. [66]: M = Pt, Pd; M' = Cr, Mo, W; L = $(CO)_3(\eta^5\text{-}C_5H_5)$; R = PPh_3, PEt_3.

high scan rates (20 V s^{-1}) whereas the first and third waves are reversible at slow scan rates (50–500 mV s^{-1}). The complex is most probably reduced to a radical anion at −1.01 V, which is in turn reduced to a dianion at −1.45 V. This anion is capable of undergoing a fast reaction such as a structural rearrangement (metal–metal bond breaking or protonation by traces of water in the solvent). The third wave could not be attributed to a definite species. The complex also shows an irreversible oxidation wave at +0.4 V.

Two trimetallic $PtCo_2$ clusters $PtCo_2(\mu\text{-}CO)(CO)_6(dppe)$ (I) and $PtCo_2(\mu\text{-}CO)(CO)_7(PPh_3)$ (II) (Fig. 9) were studied dissolved in propylene carbonate and CH_2Cl_2 at solid electrodes [63]. Both clusters undergo a one-electron irreversible reduction which leads to the release of one $Co(CO)_4^-$ anion per molecule of cluster. Among the reduction products of (II), the tetrametallic $Pt_2Co_2(\mu\text{-}CO)_3(CO)_5(PPh_3)_2$ (III) cluster was isolated in good yield (68%) and characterized. The reasonable assumption, put forward by the authors, is that the intermediate product of exhaustive electrolysis is $[PtCo(CO)_4(PPh_3)]^{\cdot}$ which rapidly dimerizes into (III). Clusters (I) and (II) also undergo two one-electron oxidation steps, observed by cyclic voltammetry. The first is reversible at high potential scans, whereas the second step leads to electrode inertness: the metallic framework is broken down upon oxidation.

Electrochemical reduction of trimetallic $[M(M'S_4)_2]^{2-}$ complexes (M = Ni^{II}, Pd^{II}, Pt^{II}; M' = Mo, W) shows [64] only two reversible one-electron reduction steps in CH_3CN containing Et_4NBr when M = Ni, M' = Mo or W. This has been interpreted as a sequential reduction at the central metal atom, according to

$$[Ni^{II}(M'S_4)_2]^{2-} \rightleftarrows [Ni^{I}(M'S_4)_2]^{3-} \rightleftarrows [Ni^{0}(M'S_4)_2]^{4-}$$

The first reduction step of the Pd(II) complexes is consistent with the formation of a Pd(I) complex, but the second reduction step is irreversible.

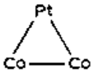
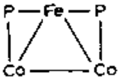
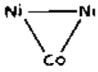
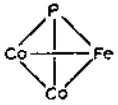
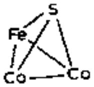
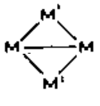
TABLE 4

Reversible oxidation states in clusters

(a) Homonuclear clusters

Cluster	Number of oxidation states and their charges	
$Fe_3(CO)_{12}$	two	$0, -1$
$[(\eta^5\text{-}C_5H_5)FeCO]_4$	four	$+2, +1, 0, -1$
$[(\eta^5\text{-}C_5H_5)FeS]_4$	five	$+3, +2, +1, 0, -1$
$[Fe_4\{S_2C_2(CF_3)_2\}_4(\mu^3\text{-}S)_4]^{2-}$	five	$0, -1, -2, -3, -4$
$[Fe_4\{S_2C_2(CF_3)_2\}_4(\mu^3\text{-}S)_4]$	five	$0, -1, -2, -3, -4$
$Fe_4(S_2C_2Ph_2)_4S_4$	two	$0, -1$
$Fe_4S_4(SR)_4$	three	$-1, -2, -3$
$[(py)_2Ru_3O(OAc)_6(pyr)]_2[Ru_3O(OAc)_6(CO)]$	ten	–
$Ni_6(\eta^5\text{-}C_5H_5)_6$	five	$+3, +2, +1, 0, -1$
$[Ni_6(\eta^5\text{-}C_5H_5)_6]^+$	six	$-2, -1, 0, +1, +2, +3$
$Co_3(\eta^5\text{-}C_5H_5)_3S_2$	four	$+2, +1, 0, -1$
$Ni_3(\eta^5\text{-}C_5H_5)_3S_2$	three	$(+\text{two})+1, 0, -1$
$Co_3(\mu^3\text{-}PPh)(CO)_9$	two	$+1, 0$
$(\eta^5\text{-}C_5H_5)Co_2C_2B_3H_5$	five	$+2, +1, 0, -1, -2$

(b) Mixed clusters

Metallic framework of the cluster	Oxidation states and charges obtained	Ref.
	$+1, 0$	63
	$0, -1$	62
	$0, -1$	109
	$0, -1$	58
	$0, -1$	67
 (M = Pt, Pd) (M' = Cr, Mo, W)	$+1, 0$	66

The Pt(II) complexes showed a simultaneous two-electron reduction leading to formally zerovalent Pt(0) complexes. For a review on transition metal thiometallates including electrochemical data, see ref. 65.

A series of tetrametallic clusters (Fig. 10) has been studied in DMF containing 0.1 M TEAP at a platinum electrode [66]. These planar $M_2M'_2L_n$ clusters undergo a single two-electron irreversible reduction leading to destruction of the metallic framework. They also show two oxidation steps. The first one-electron step corresponds to an electrochemical–chemical mechanism. The second step is totally irreversible.

Electrochemical data on the mixed $SFeCo_2$ cluster [67] are given in Section E.

$Co_4(CO)_{12}$ is reduced at a more positive potential than the related complex $HRuCo_3(CO)_9$, replacement of a Co by a Ru atom in the metallic framework reinforces the tendency of the cluster towards reduction [66].

In conclusion, a series of highly symmetrical homonuclear clusters with strong metal–metal bonds exhibits specific redox behaviour in that (a) they show multiple and numerous oxidation states (from two to ten), (b) they most often exhibit reversible one-electron transfers, (c) they remain intact in more than one molecular oxidation state. Examples of several clusters are listed in Table 4. A common feature of most of these clusters is the metallic framework surrounded by strong π-bonding ligands such as η^5-C_5H_5. A correlation of this behaviour may be drawn with the mononuclear analogs; for instance ferrocene [68] or dibenzenechromium [69] are also reversibly oxidized. Most of these clusters are derived from the chemistry of metallocenes for which the metallic core is "shielded" from destruction by π ligands. As can be seen in Table 4, comparison between the reversible oxidation states exhibited by homogeneous and mixed-metal clusters provides no general rules as yet. The former species show a greater tendency to multiple oxidation states than the latter. Charge delocalization on suitable ligands favors the former series. In contrast, mixed-metal clusters break down in solution over a redox range involving variation of numerous valence electrons. The dissymmetry introduced by the mixed nature of the metallic framework either weakens or reinforces its cohesion. Additional electrochemical studies should enable us to obtain a more general view of this subject.

E. PARAMAGNETIC ELECTROCHEMICALLY GENERATED CLUSTER SPECIES

It has been shown that clusters often undergo oxidation or reduction by single electron-transfer steps. Therefore, it is essential to combine the technique of ESR spectroscopy with electrolysis. A number of paramagnetic cluster species has been obtained, particularly radical anion clusters. Many of these are stable radical anions.

In Section C, it was reported that the radical anion $[Fe_3(CO)_{12}]^{\dot{-}}$ ($g = 2.051$, 2.003) was obtained over a definite temperature range. The same authors [31] have also reported the following radical anions: $Fe_3(CO)_{11}P(OPh)_3^{\dot{-}}$, $g = 2.052$, 2.003; $RuFe_2(CO)_{12}^{\dot{-}}$, $g = 2.053$, 2.004; $Ru_3(CO)_{12}^{\dot{-}}$, $g = 1.982$; $Os_3(CO)_{12}^{\dot{-}}$, $g = 2.001$; $Ir_4(CO)_{12}^{\dot{-}}$, $g = 2.002$; $Ru_6C(CO)_{17}^{\dot{-}}$, $g = 2.001$; together with other metal carbonyl radical anions which illustrate the generality of one-electron reduction in solution of these carbonyl complexes. The variation with temperature of the ESR spectra may indicate fluxional behavior of these species. The lifetimes of heavy-metal anions were at least several hours but attempts to isolate solid salts failed.

Four paramagnetic anions were characterized by their ESR spectra: $Fe(CO)_4^{\dot{-}}$; $Fe_2(CO)_8^{\dot{-}}$; $Fe_3(CO)_{11}^{\dot{-}}$; $Fe_4(CO)_{13}^{\dot{-}}$. These anions were obtained by chemical reduction and their existence suggests an important role for a one-electron pathway in the chemistry of iron carbonyl compounds [70,71]. ESR spectra of $Fe_3(CO)_{12}$ electrochemically generated radicals are reported by Vlcek and co-workers [33] and confirm the results previously obtained by Peake et al. [31].

(i) Cobalt clusters

Twelve complexes of the type $XCCo_3(CO)_9$ (Fig. 11) ($X = H$, halogen, alkyl, aryl, etc.) were studied [72] dissolved in CH_2Cl_2 containing 0.2 M TBAP. These clusters generally undergo a reversible one-electron reduction in the range -0.7 to -0.9 V vs. SCE, depending on the nature of the substituent X. The more electronegative substituents induce a reduction potential near -0.7 V. These clusters were reduced and their ESR spectra recorded and found to consist of at least 16 lines with a hyperfine splitting constant of 35.9 G (for $X = Cl$). The spectrum changed only slightly with a change in the substituent. Multistep oxidations of these clusters were also studied.

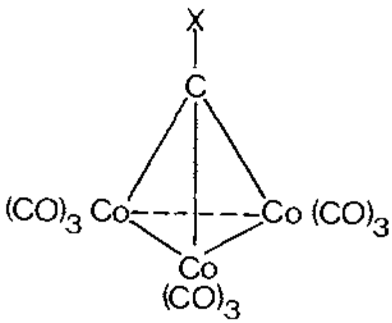


Fig. 11. The clusters studied by Kotz et al. [72] ($X = H$, halogen, alkyl, aryl, etc.).

The small change in the ESR spectrum with change of substituent suggested that the LUMO encompassed three equivalent cobalt atoms and that there is only small, if any, spin density leakage from the core to the substituent.

A series of papers by Bond et al. [32,67,73–75] devoted to "paramagnetic organometallic molecules" appeared recently, some of which are concerned with cluster electrochemistry and particularly with the methinyltricobalt enneacarbonyls. The complexes $XCCo_3(CO)_9(X = Me, Et, Ph, H, F, CF_3, Cl, Br, CF_3CH_2$, etc) undergo one-electron reduction to produce stable radical anions where the cluster structure is retained [73]. Certain of these, such as $PhCCo_3(CO)_9^{\dot{-}}$ and $MeCCo_3(CO)_9^{\dot{-}}$, show particularly long lifetimes (several hours). The g values (near 2.0) are close to the free-electron value, from which it is inferred that the unpaired electron resides in a non-degenerate orbital. This is in accordance with conclusions of ESR studies on the chalcogen clusters $FeCo_2(CO)_9S$ and $Co_3(CO)_9S$. Hyperfine coupling to the three cobalt nuclei is observed, but hyperfine interactions with the apical carbon nucleus and apical substituent nuclei are absent.

In acetone containing 0.1 M TEAP, the $E_{1/2}$ values of the couple $XCCo_3(CO)_9/XCCo_3(CO)_9^{\dot{-}}$ have been found to be in the range -0.2 to -0.5 V vs. Ag/Ag^+, depending on the nature of X [74]: the most difficult clusters to reduce are those with electron-donating apical substituents. The $E_{1/2}$ values have been correlated with the charge density on the cobalt atoms in neutral complexes but when X is a halogen simple inductive arguments do not explain the $E_{1/2}$ shifts. The authors therefore invoked a mesomeric component in the bonding to the apical substituent.

The radical anion is in turn irreversibly reduced at potentials near the solvent limit, even at 193 K, and there is evidence for destruction of the cluster unit according to the following sequence

$$\begin{tikzcd} PhCCo_3(CO)_9 \arrow[r, "-0.45\ V", "1e^-"', shift left] & \arrow[l, shift left] [PhCCo_3(CO)_9]^{\dot{-}} \arrow[r, "1e"'] & [PhCCo_3(CO)_9]^{2-} \arrow[d] \\ & & Co(CO)_4^- + ? \end{tikzcd}$$

These clusters were not oxidized in the potential range available. Further electrochemical studies [75] were undertaken by the same authors at Hg and Pt electrodes on similar ligand-substituted clusters $XCCo_3(CO)_{9-n}L_n$ [$n = 1$–3; $L = PR_3, P(OR)_3$, CNR]. In these cases, a one-electron series does exist (provided the right ligand is used) with the formal oxidation states $+1$, 0, -1. For the monosubstituted series, a reversible one-electron reduction is observed at 203 K. As more CO groups are replaced by Lewis bases, reduction becomes progressively more difficult while oxidation becomes easier. Thus, when $n = 2$ irreversible oxidations are observed, whereas when $n = 3$ both reversible oxidations and reductions are found. The electrode processes are represented by the following schemes

$$\text{Reduction:}\quad \mathrm{XCCo_3(CO)_{9-\mathit{n}}L_\mathit{n} + e^- \rightleftarrows XCCo_3(CO)_{9-\mathit{n}}L_\mathit{n}^{\cdot -}}$$

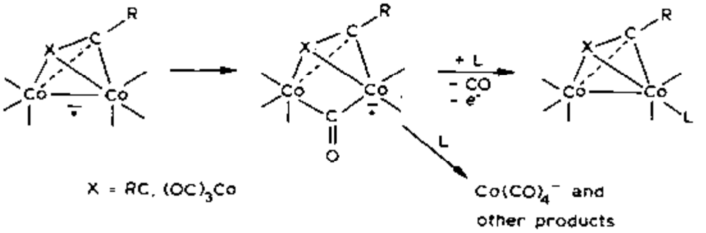
$$\mathrm{XCCo_3(CO)_{9-\mathit{n}}L_\mathit{n}^{\cdot -} \rightarrow Co(CO)_4^- + XCCo_3(CO)_9^{\cdot -}}$$

$$+\text{other products}$$

Formation of the unstable dianions $[\mathrm{XCCo_3(CO)_{9-\mathit{n}}L_\mathit{n}}]^{2-}$, either by electrolysis or by disproportionation of the radical anion, liberates CO which initiates ligand replacement. A mechanism of dismutation of the radical anion has been proposed. ESR spectra on frozen radical anion solutions showed the $\mathrm{Co_3C}$ cluster to be only slightly perturbed by replacement of a CO group by a Lewis base.

No ESR signal could be detected for the cation $[\mathrm{XCCo_3(CO)_6L_3}]^+$ produced when $n = 3$, in spite of the fact that it should be paramagnetic.

The reactivity of the radical anions has also been investigated. Rieger and co-workers [76] with similar clusters [$\mathrm{PhCCo_3(CO)_9}$, $\mathrm{PhCCo_3(CO)_8PPh_3}$ and other compounds] observed that electrolytically generated radical anions react rapidly with phosphine or phosphite nucleophiles and that the substituted intermediate is rapidly oxidized to the final products. The substitution slows down as the temperature is lowered. It is expected that these electron-induced nucleophilic substitutions will be adaptable to homogeneous reaction conditions. The following scheme was proposed to explain the cyclic voltammetric data [76]



(ii) Mixed iron–cobalt clusters

Another mixed cluster $\mathrm{SFeCo_2(CO)_9}$ has been reduced in acetone at both Pt and Hg electrodes [67]. Three waves were obtained at −0.24, −0.92 and −1.75 V vs. Ag/AgCl. The first two waves are one-electron reductions. The first step is represented as

$$\mathrm{SFeCo_2(CO)_9 + e^- \rightarrow SFeCo_2(CO)_9^{\cdot -}}$$

whereas the second step corresponds to an irreversible process due to fragmentation of the cluster. The related clusters $(CO)_5Cr{-}SFeCo_2(CO)_9$ and $SFeCo_2(CO)_8P(OPh)_3$ were also studied for comparison purposes. The chemically or electrochemically generated radical anion has a half-life of 1 min at ambient temperature. Frozen ESR spectra of $SFeCo_2(CO)_9^{\dot{-}}$ were compared with those of the non-substituted $XCCo_3(CO)_9^{\dot{-}}$ and interpreted in terms of anisotropic g and cobalt hyperfine tensors. Replacement of Co by Fe in the cluster results in a net gain in cobalt spin density (approximately 60% on the two cobalt atoms).

As is apparent from the recent literature, the field of paramagnetic clusters is progressively expanding and there is no doubt that the reactivity of radical anions will give rise to new possibilities. It is likely that these radical species obtained either by chemical or by electrochemical reduction, as well as by photochemical reactions, may play an important role in the comprehension of cluster formation, cluster reactivity and cluster applications.

F. REDOX BEHAVIOUR OF METAL–HALIDE AND METAL TETRATHIOLENE CLUSTERS

(i) Metal–halide clusters

Clusters of general formula $(M_xX_y)^{n+}$, where M is a transition metal such as Nb, Ta, Mo, W, Re and X is a halogen, were extensively studied by Kendworth and Walton [77]. Electrochemistry was only one technique complementary to many others. Consequently, the electrochemical data on these types of compounds are scarce and fragmentary. However, it is evident, from the chemical results, that the redox behaviour of $(M_xX_y)^{n+}$ must give rise to a rich electrochemistry.

Nb and Ta clusters

The complex $(Nb_6Cl_{12})^{2+}$ undergoes a two-electron oxidation when titrated with iodine or oxidized polarographically [78,79]. For the related (Ta_6Cl_{12}) cluster, oxidation states of +2, +3 and +4 have been found in aqueous solutions and solid derivatives of the +4 ion have been isolated. Thus, approximately 10^{-3} M solutions of $Nb_6Cl_{17}\cdot 7\ H_2O$ in 1 M $KClO_4$ gave a polarographic wave at $E_{1/2} = +0.426$ V vs. a hydrogen electrode, corresponding to the reaction

$$(Nb_6Cl_{12})^{2+} \rightleftharpoons (Nb_6Cl_{12})^{4+} + 2\ e^-$$

In 0.5 M potassium oxalate acidified by HCl, the anodic wave appears at $E_{1/2} = +0.341$ V vs. the same reference electrode: the oxidation product is complexed by the oxalate to a greater degree than is $(Nb_6Cl_{12})^{2+}$.

TABLE 5

Results of Kendworth and Walton [77] on Nb and Ta clusters

Cluster	$E_{\mathrm{red}}^{1/2\,\mathrm{a}}$	$E_{\mathrm{ox}}^{1/2\,\mathrm{a}}$	
$(Nb_6Cl_{12})Cl_2(PEt_3)_4$	−0.99	+1.09	+0.53
$(Nb_6Cl_{12})Cl_2(P\text{-n-}Pr_3)_4$	−1.00	+1.09	+0.53
$(Nb_6Cl_{12})Cl_2(PEt_2Ph)_4$	−0.98	+1.09	+0.53
$(Ta_6Cl_{12})Cl_2(P\text{-n-}Pr_3)_4$	~−1.4	+0.77	+0.19

[a] 0.2 M TBHP, CH_2Cl_2, V vs. SCE, Pt electrode.

The Ta cluster $(Ta_6Br_{12})^{2+}$ was studied by Kuwana and co-workers [80]. In aqueous 0.1 M $HClO_4$ solutions this species shows two consecutive reversible one-electron transfer steps at +0.35 and +0.65 V vs. SCE at 25°C. The $(Ta_6Cl_{12})^{2+}$ cluster behaves similarly to the bromide analog ($E_1 = +0.25$ and $E_2 = +0.59$ V vs. SCE). During electron transfer a slight structural change occurs upon oxidation, particularly between the +2, +3 and +4 cluster ions.

Hydrated niobium and tantalum chloride clusters $M_6Cl_{14} \cdot 8\ H_2O$ and $M_6Cl_{15} \cdot 7\ H_2O$ react with PR_3 (R = alkyl or aryl group) to give $(M_6Cl_{12})Cl_2(PR_3)_4$ [77]. Their redox behaviour, summarized in the following equation, reveals the existence of the couples

$$(M_6Cl_{12})Cl_2(PR_3)_4 \underset{+e^-}{\overset{-e^-}{\rightleftarrows}} [(M_6Cl_{12})Cl_2(PR_3)_4]^+ \underset{+e^-}{\overset{-e^-}{\rightleftarrows}} [(M_6Cl_{12})Cl_2(PR_3)_4]^{2+}$$

The half-wave potentials are collected in Table 5. The phosphine ligands have a great tendency to stabilize the lower oxidation states in these clusters. They also favor the solubility of the resulting complexes in non-aqueous media.

Niobium and tantalum halide clusters of the type $(M_6X_{12})^{n+}$ ($n = 2$–4) undergo one-electron redox reactions in which the cluster structure is preserved. This is not the case for Mo(II) and W(II) halide clusters.

Mo and W clusters

Almost all Mo and W halide clusters of type $(M_6X_8)^{4+}$ show irreversible oxidation with destruction of the cluster structure. An exception is $(W_6Br_8)Br_4$, which leads to derivatives of $(W_6Br_8)^{6+}$ [81,82]. Chlorine oxidation of $(Mo_6Cl_8)Cl_4$ and $(W_6Cl_8)Cl_4$ leads respectively to the species $(Mo_6Cl_{12})Cl_3$ and $(W_6Cl_{12})Cl_6$ [83,84]. Chemical oxidation of $(M_6X_8)X_4$ similarly has not revealed any redox behaviour in which a cluster structure is preserved [85,86]. The only exception is that of $(Mo_6Cl_8)Cl_4$ [87] which reacts with tertiary phosphines to give an unknown cluster. This first ligand-induced reaction [87] of $(Mo_6Cl_8)^{4+}$ {as present in $(Mo_6Cl_8)Cl_4$ and

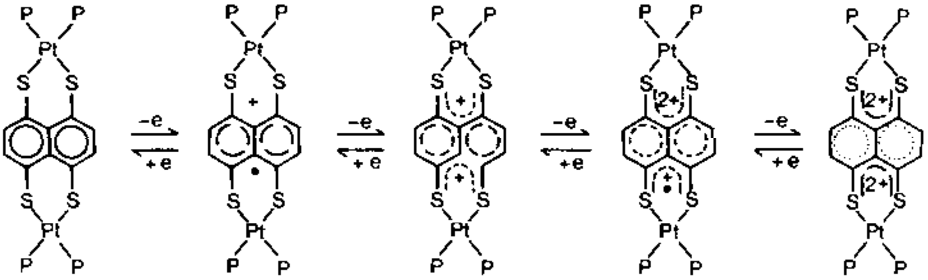


Fig. 12. Five reversible oxidation states studied by Teo et al. [89].

$[(Mo_6Cl_8)X_6]^{2-}$ where X = Cl, Br, I} leads to $(Mo_6Cl_8)^{2+}$. The published results concern only chemical oxidation–reduction; no electrochemical studies have been undertaken.

Luminescence and redox photochemical studies of the Mo(II) cluster $(Mo_6Cl_{14})^{2-}$ have been performed by Maverick and Gray [88]. Cyclic voltammetry on $(Bu_4N)_2(Mo_6Cl_{14})$ in CH_3CN reveals a nearly reversible, diffusion controlled, one-electron oxidation step at 1.29 V vs. Ag/0.1 M Ag^+, a potential 0.6 V more positive than that for oxidation of Cl^-.

Studies of the rhenium clusters have, to date, only concerned their chemical reactions.

(ii) Metal tetrathiolene complexes

Teo et al. [89–91] have carried out extensive studies on a new class of organochalcogen compound containing one or two chalcogen–chalcogen bonds used as ligands in organometallic synthesis (Fig. 12). Molecular complexes containing two, four and six metal atoms were obtained. A new class of organometallic polymers based on these ligands has also been synthesized. These complexes, which were described as clusters by the authors, show interesting properties: rich electrochemistry, unusual stereochemistry and semiconducting properties. They can be used as reversible anode materials in a rechargeable battery system [91].

The initial report [89] of the electrochemistry of a new platinum dimer shows that it may be oxidized in four reversible one-electron steps (Fig. 12). The mono-, di-, tri- and tetra-cations are obtained. The paramagnetic mono- and tri-cations showed ESR spectra indicating that the electrons are being removed from a predominantly central ligand-based MO.

Complexes of the type $(PPh_3)_4Pt_2(L)$ where L = TTL (tetrathiolene), TTT (tetrathiotetracene), TTN (tetrathionaphthalene), TCTTN (tetrachlorotetrathionaphthalene), have been investigated [90] by cyclic voltammetry at a platinum electrode in CH_2Cl_2 containing 0.1 M TBAP. The complex

$(PPh_3)_4Pt_2(TTT)$ oxidizes in two, one-electron reversible steps at −0.51 and −0.28 V while $(PPh_3)_4Pt_2(TTN)$ shows four reversible one-electron oxidation waves at −0.28, ≈0.05, 0.01 and 0.31 V (Fig. 12). The complex $(PPh_3)_4Pt_2(TCTTN)$ exhibits two reversible one-electron oxidations at −0.02 and 0.21 V as well as two quasi-reversible waves at 0.58 and 0.98 V (vs. Ag/0.01 M $AgNO_3$). These potentials are compared and correlated with the oxidation potentials of the free tetrathiolene ligands and the potential shifts between the free ligands and the metal complexes discussed in terms of MO energies.

New data for molecular complexes containing more than two platinum atoms should develop these initial results, in particular, in the field of organometallic polymers.

G. ELECTROCHEMICAL APPLICATIONS OF CLUSTERS: ELECTROCATALYSIS, BIOLOGICAL ASPECTS, CHARGE-TRANSFER COMPLEXES, ELECTROSYNTHESIS

(i) Electrocatalysis by clusters

Under specific experimental conditions, highly dispersed bimetallic and trimetallic catalysts of Pt, Ru and Cu may be prepared on a carbon support [92]. The electrochemical properties of these preparations have been studied by cyclic voltammetry which indicates that the concept of an "alloyed catalyst" may be applied with Cu forming a chemisorbed surface layer on Pt, Ru and Pt/Ru crystallites. The role of copper in reducing the capacity of Pt and Ru, both separately and combined, to incorporate hydrogen has been confirmed.

Electroreduction of dinitrogen into N_2H_4 and NH_3 in a medium containing a homogeneous catalytic system comprising Ti(III) and Mo(III) alkoxide clusters has been achieved on a mercury cathode [93,94]. It was shown that the rate-determining step is electron transfer to the dinitrogen molecule in the coordination sphere of the catalyst in contact with mercury.

It has been suggested [95] that the cluster $Co_3(CO)_9COH$ is a model for hydrogenation of CO to MeOH in homogeneous and heterogeneous phases. Until now, electrocatalytic studies on such compounds have not been undertaken; they would probably provide interesting results, however.

(ii) Biological aspects of cluster electrochemistry

The first studies on the Fe–S proteins involved the measurement of redox potentials in aqueous solutions. These were compared with their Fe_4 active site synthetic analogs in non-aqueous media. A substantial negative shift of the latter potentials compared to the former was observed. A recent study

[96] compares the polarographic potentials of the synthetic analog $[Fe_4S_4(SR)_4]^{2,3-}$ (Fig. 13) with that of the "Clostridium pasteurianum" ferredoxin Fd_{ox}/Fd_{red} redox couples, at a dropping mercury electrode, in the same solvent media, which ranged from 80% Me_2SO/H_2O (v/v) to pure water (pH = 8.4). The results indicate that the protein is reduced by a reversible one-electron transfer, and that the $E_{1/2}$ values of $[Fe_4S_4(SR)_4]^{2,3-}$ increase from 80% Me_2SO to water. In the 80 to ca. 40% Me_2SO range, the positive potential shift of the couple Fd_{ox}/Fd_{red} also changes monotonically (from -0.93 to -0.70 V), but remains invariant from 60% to the pure aqueous limit. An interpretation of this shift in $E_{1/2}$ is that progressive solvation by water in the analogous systems occurs as the aqueous content is increased. Similar behaviour occurs for the protein in solvents down to 40% Me_2SO, but at $\leqslant 40\%$ Me_2SO, the protein reverts to its normal aqueous solution structure, shielding the active sites from solvent effects. The different factors which might cause the potential differences $\Delta E_{1/2} = E_{1/2(\text{analog})} - E_{1/2}(\text{Fd})$ in the same medium have been discussed.

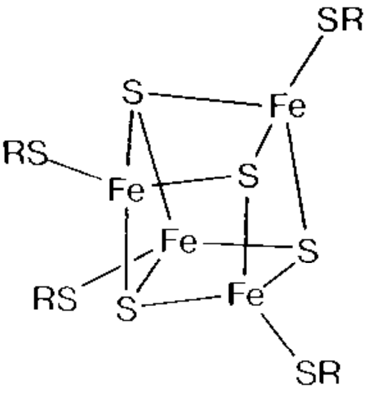


Fig. 13. Fe_4S_4 cores in analogs of protein-active sites, studied by Holm and co-workers [96].

The protein molecule studied contained two separate and essentially equivalent Fe_4 sites in a protein structure. Participation of the ferredoxin reaction center in its electrochemical reduction has been described [97]. The role of some cubane-like clusters in nitrogenase is also of interest and at least two papers related to electrochemistry on this subject have been published [98,99]. The Fe_3MoS_4 cubane-like cluster core in the $[Fe_6M_2S_8(SR)_9]^{3-}$ (M = Mo, W) anions represents the best synthetic analog to date for the molybdenum centre of nitrogenase. The electrochemical behaviour of these systems is similar to that expected for two Fe_4S_4 cubane-like clusters linked by slight inter-cluster coupling. It has been reported by Garner et al. [98,99]

that $[Fe_6Mo_2S_8(SEt)_9]^{3-}$ shows good electrochemical reversibility in DMSO for the couples $3-/4-$ and $4-/5-$, whereas with the similar tungsten anion $[Fe_6W_2S_8(SEt)_9]^{3-}$ these redox couples appear to be irreversible. Recent studies in CH_3CN show these redox couples to be reversible but their reversibility is solvent dependent. The roles of Mo and W in nitrogenase was discussed in these models. In particular the failure of W to produce a functional nitrogenase may arise from the sensitivity of this atom towards attack by oxygen-donor ligands. The electron-transfer kinetics may therefore be altered together with this center in dinitrogen reduction. Polarographic studies on proteins are reviewed in ref. 101.

(iii) Charge-transfer complexes

Reversible topotactic electron/proton transfer reactions of the type

$$xH^+ + xe^- + Z \rightleftharpoons H_x^+(Z)^{x-} \quad (Z = \text{host lattice matrix})$$

in molecular solids have been studied electrochemically and structurally in the cases of [100]: (i) $[Pt(NH_3)_4]^{2+}[PtCl_4]^{2-}$; (ii) $Ta_6Cl_{14} \cdot 8\,H_2O$; and (iii) $(QH)^+[(TCNQ)_2]^-$ (quinolinium tetracyanoquinodimethane). The results obtained are summarized in the following equations

$$[Pt(NH_3)_4PtCl_4]^{0.5+}(H_{1.5}SO_4)^{0.5-}(H_2O)_y \rightleftharpoons [Pt(NH_3)_4PtCl_4]^{(0.5+x)+}$$

$$(H_{1.5-x}SO_4)^{(0.5+x)-}(H_2O)_y + xH^+ + xe^-$$

$$(Ta_6Cl_{14})(H_2O)_8 \rightleftharpoons (Ta_6Cl_{14})^{x+}(OH^-)_x(H_2O)_{8-x} + xe^- + xH^+$$

$$(QH^+)[(TCNQ)_2]^- + xH^+ + xe^- \rightleftharpoons (QH^+)(H^+)_x[(TCNQ)_2]^{(1+x)-}$$

These topotactic reactions are of synthetic interest and are relevant to modifications of the physical properties of molecular solids.

(iv) Electrosynthesis of clusters

Previous studies [102–104] on organometallic compounds have shown that it is possible to obtain a dinuclear complex from a mononuclear complex, by electroreduction {e.g. $Fe(CO)_5$ gives $[Fe_2(CO)_8]^{2-}$; $Cr(CO)_6$ gives $[Cr_2(CO)_{10}]^{2-}$}. An increase in nuclearity was also observed with $M_2(CO)_{10}$ which gives after electroreduction $[M_3(CO)_{14}]^-$ ($M = Mn$, Re) [105]; similarly $PtCo_2(\mu\text{-}CO)(CO)_7(PPh_3)$ leads to $Pt_2Co_2(\mu\text{-}CO)_3(CO)_5(PPh_3)_2$ [63]. The electrochemically catalyzed replacement of the carbonyl ligand by $P(OMe)_3$ in the cluster $Fe_3S_2(CO)_8L$ ($L = C_3H_2S_2$) proceeds stepwise and leads to the new clusters $Fe_3S_2(CO)_{8-n}L\{P(OMe)_3\}_n$ ($n = 1$–3) [106]. Therefore, electrosynthesis is a feasible alternative to pyrolysis and photolysis for the manufacture of clusters, in spite of the fact that only a few such studies have been undertaken to date.

Clusters such as $K_4Nb_6Cl_{18}$ and $Gd_5Cl_5C_2$ have been obtained recently by molten salt electrolyses [107] showing that electrochemical reduction of transition metal halides is a promising method for the preparation of metal-rich compounds.

Grobe and Schneider [108] described the electrochemical synthesis of Fe, Co and Ni carbonyl compounds using metal anodes from the corresponding acetylacetonates in oxidation states +2 and +3. Solvent effects and the problems of cluster formation during electrolysis were discussed.

H. CONCLUSION

The discovery of new reversible redox systems is of general interest: the redox potentials do not differ greatly from the formal potentials. The influence of the nature of the ligand on $E_{1/2}$ is often discussed. Unfortunately no kinetic data are available for these systems. The net result of the loss or gain of one electron is to modify the number of valence electrons involved in the cluster and therefore the metal–metal bond length. Electronic exchange is interpreted either as a weakening of the metal–metal bond when an antibonding LUMO is involved (electroreduction) or as a reinforcement of the metal–metal bond when a bonding HOMO is concerned (electro-oxidation). Generally, the greater the number of electrons in a cluster, the greater the number of reversible oxidation steps that will occur before destruction of the complex. This also depends largely on the nature of the ligands attached to the metallic core; ligands with delocalized electrons favour stable ionic species. The concept of "electron reservoir" holds for such clusters,

A number of clusters show irreversible redox steps. As a consequence, the metallic framework is destroyed after electron exchange. This is the case for weak metal–metal bonded complexes or for species surrounded by non-stabilizing ligands (e.g. compare the ligand CO with diphenylphosphinoethane). The redox potentials then include not only a thermodynamic but also a kinetic contribution which may be substantial. It could be important to identify the cluster fragments obtained after electrolysis, in spite of the fact that they can react with the solvent or other species in solution. Often, ESR coupled with coulometry affords the possibility of detecting paramagnetic intermediates with short lifetimes.

For the purposes of catalytic reactivity, it now seems that neutral clusters which have gained or lost one or more electrons are more active than the parent species, although the metallic framework is often less stable in ionic species.

Initial studies on cubane-like metal clusters suggest a new method for preparing homologous complexes with varying numbers of electrons. The Fe_4S_4(cysteine)$_4$ cluster is found at the active site of the bacterial ferredoxins as well as at that of the high-potential iron protein isolated from chromatium. The biological applications of cluster electrochemistry should therefore be further explored together with the topics of electrosynthesis of clusters and electrocatalysis by clusters.

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