

## TRENDS IN REDOX POTENTIALS OF TRANSITION METAL COMPLEXES \*

H.L.M. VAN GAAL and J.G.M. VAN DER LINDEN

*Department of Inorganic Chemistry, Catholic University, Toernooiveld, 6525 ED Nijmegen  
(The Netherlands)*

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### A. INTRODUCTION

The trend in standard electrode potentials for  $M(H_2O)_6^{2+}$  complexes has been reasonably reproduced by thermodynamic calculations [2] in which the influence of ligand field contributions has been incorporated and a correlation with ionisation potentials has been recognised [3–5]. Ligand field energies have also been considered for other metal based redox systems. Kim and Rock [6] have established a correlation between  $Dq$  values and redox potentials for a series of octahedral cobalt and iron complexes. Chadwick and Sharpe [7] used a ligand field energy calculation for a comparison of the redox potentials of the oxidations of  $M(H_2O)_6^{2+}$  and  $M(CN)_6^{4-}$  ( $M = Cr, Mn, Fe, Co$ ), although the agreement with experimental values was only moderate. Lintvedt and Fenton [8] stressed the importance of the spherical ligand field energy term in addition to other ligand field contributions to the  $E^\circ$  of transition metal complexes. In general, neither the full thermodynamic treatment, nor the more restricted ligand field treatment has resulted

\* See ref. 1.

TABLE 1

 $E^\circ(E_{1/2})$  values (V) for metal complexes of the first transition series

Compound	Oxidation	V	Cr	Mn	Fe	Co	Ni
$M(H_2O)_6^{2+/3+ a}$	(II/III)	-0.25	-0.41	+1.54	+0.77	+1.84 <sup>t</sup>	-
$M(acac)_3^{1- / 0 b}$	(II/III)	-	-1.13	+0.64	+0.07	+0.30 <sup>t</sup>	-
$M(dtc)_3^{0/1+ c}$	(III/IV)	+0.70 <sup>d</sup>	+1.10 <sup>e</sup>	+0.41 <sup>f</sup>	+0.55 <sup>g</sup>	+1.10 <sup>e</sup>	+0.36 <sup>h</sup>
$M(dtc)_3^{1- / 0 c}$	(II/III)	-0.77 <sup>d</sup>	-1.48 <sup>e</sup>	-0.07 <sup>f, i</sup>	-0.38 <sup>g, t</sup>	-0.92 <sup>e</sup>	-0.61 <sup>h</sup>
$M(bipy)_3^{2+/3+ i}$	(II/III)	-	-0.23 <sup>j</sup>	-	+1.06 <sup>k</sup>	+0.31 <sup>k</sup>	+1.71 <sup>l</sup>
$M(bipy)_3^{1+/2+ i}$	(I/II)	-1.01 <sup>j</sup>	-0.70 <sup>j, k</sup>	-	-1.26 <sup>m, t</sup>	-0.88 <sup>k</sup>	-1.29 <sup>l</sup>
$M(CN)_6^{4- / 3- n}$	(II/III)	-	-1.28	-0.24	+0.36	-0.80 <sup>t</sup>	-
$M(C_5H_5)_2^{0/1+ o}$	(II/III)	-0.55 <sup>p</sup>	-0.67 <sup>p</sup>	-	+0.42 <sup>q</sup>	-0.98 <sup>q</sup>	-0.09 <sup>p</sup>
$M(C_5H_5)_2^{1- / 0 o}$	(I/II)	-2.74 <sup>p</sup>	-2.30 <sup>p</sup>	-	-2.93 <sup>r</sup>	-2.05 <sup>q</sup>	-1.66 <sup>p</sup>
$M_2(C_{10}H_8)^{1+/2+ s}$	(II/III)	+0.14	-0.18	-	+0.72	-0.07	+0.12
$M_2(C_{10}H_8)^{0/1+ s}$	(II/III)	-0.09	-0.84	-	+0.13	-0.95	-0.29

<sup>a</sup> Ref. 9(c), V vs. SHE. <sup>b</sup> G. Gritzner, H. Murauer and V. Gutmann, J. Electroanal. Chem. Interfacial Electrochem., 101 (1979) 177 [in  $CH_3CN$  vs. the  $Cr(C_6H_5)_2^{0/1+}$  couple]. <sup>c</sup> In acetone vs. Ag-AgCl, 0.1 M LiCl electrode, or corrected. <sup>d</sup> T.L. Riechel, L.J. Dehayes and D.T. Sawyer, Inorg. Chem., 15 (1976) 1900 (measured in  $CH_3CN$  vs. SCE, correction 0.25 V). <sup>e</sup> R. Chant, A.R. Hendrickson, R.L. Martin and N.M. Rohde, Aust. J. Chem., 26 (1973) 2533. <sup>f</sup> A.R. Hendrickson, R.L. Martin and N.M. Rohde, Inorg. Chem., 13 (1974) 1933. <sup>g</sup> R. Chant, A.R. Hendrickson, R.L. Martin and N.M. Rohde, Inorg. Chem., 14 (1975) 1894. <sup>h</sup> J.G.M. van der Linden and A.H. Dix, Inorg. Chim. Acta, 35 (1979) 65. <sup>i</sup> In DMF vs. SCE, or corrected. <sup>j</sup> Ref. 16. <sup>k</sup> T. Saji and S. Aoyagi, J. Electroanal. Chem. Interfacial Electrochem., 60 (1975) 1. <sup>l</sup> R. Prasad and D.B. Scaife, J. Electroanal. Chem. Interfacial Electrochem., 84 (1977) 373 (measured in  $CH_3CN$  vs. Ag/AgNO<sub>3</sub>, correction 0.26 V). <sup>m</sup> T. Saji and S. Aoyagi, J. Electroanal. Chem. Interfacial Electrochem., 58 (1975) 401. <sup>n</sup> Ref. 7, V vs. SHE. <sup>o</sup> All values for metallocenes vs. SCE. <sup>p</sup> J.D.L. Holloway and W.E. Geiger, Jr., J. Am. Chem. Soc., 101 (1979) 2038. <sup>q</sup> S.P. Gubin, S.A. Smirnova and L.I. Denisovich, J. Organomet. Chem., 30 (1971) 257 (in  $CH_3CN$  vs. SCE). <sup>r</sup> Y. Mugnier, C. Moise, J. Tirouflet and E. Laviron, J. Organomet. Chem., 186 (1980) C49 (in DMF vs. SCE). <sup>s</sup> Ref. 19, V vs. SCE. <sup>t</sup> Special cases, for comments see text.

TABLE 2

 $E_{1/2}$  values (V) of some 1,2-dithiolenes of the first transition series <sup>a</sup>

Compound	Oxidation state	Ti	V	Cr	Mn	Fe	Co
$M(S_2C_6Cl_4)_3^{2-/-1-}$	(IV/V)	+0.58 <sup>b</sup>	+0.17	+0.11	+0.40	+0.27	-
$M(S_2C_6Cl_4)_3^{3-/-2-}$	(III/IV)	-1.05	-0.97	-0.36	-0.92	-0.77	-
$M(S_2C_6Cl_4)_3^{4-/-3-}$	(II/III)	-	-	-	-1.12 <sup>b</sup>	-1.51	-
$M[S_2C_2(CN)_2]_3^{2-/-1-}$	(IV/V)	-	+0.48	+0.76	-	+0.53	+0.40 <sup>b</sup>
$M[S_2C_2(CN)_2]_3^{3-/-2-}$	(III/IV)	-	-0.61	+0.05	-0.35	-0.38	+0.03
$M[S_2C_2(CN)_2]_3^{4-/-3-}$	(II/III)	-	-	-	-0.72 <sup>b</sup>	-1.18	-

<sup>a</sup> In  $CH_2Cl_2$  vs. SCE. Data taken from ref. 15. <sup>b</sup> Special cases, for comments see text.

in a satisfactory insight into the relationships between redox potentials and metal characteristics such as electron configuration. Textbooks presenting such relationships are rather cloudy about their origin [4,9].

In this article a model is developed to evaluate the relative  $d$  orbital energies in transition metal containing redox systems and using this model trends in redox potentials are discussed. Redox potentials have been successfully related to the energy of the redox orbital for organic systems [10] as well as for organometallic systems [11] by means of molecular orbital calculations. Experimental evidence that such relations exist comes from published correlations between  $E_{1/2}$  values and charge-transfer energies [12].

In the last decade a wealth of redox data on dithiocarbamate ( $dtc = R_2NCS_2^-$ ) complexes has appeared [13]. Together with the data on aquo complexes, they provide a good starting point for the evaluation of  $d$  orbital energy contributions to  $E^\circ$  values [14]. The model is also applied to other series of octahedral or pseudo-octahedral complexes containing various ligand systems with the emphasis on common aspects of these complexes in relation to their redox properties.

$E^\circ$  and  $E_{1/2}$  data from the literature are given in Tables 1 and 2.

## B. RELATIVE REDOX POTENTIALS

The redox processes considered here are the one-electron oxidations and reductions of the octahedral transition metal complexes  $ML_x^z$ :  $ML_x^z \rightarrow ML_x^{z+1} + e^-$ , with standard electrode potential  $E_{ox}^\circ(n, z) = E^\circ(n, z)$ ;  $ML_x^{z-1} \rightarrow ML_x^z + e^-$ , with the standard electrode potential  $E_{red}^\circ(n, z) = E^\circ(n+1, z-1)$ , where  $z$  is the charge of the complex and  $n$  is the number of  $d$  electrons on the central metal atom.

Discussion of trends implies discussion of differences and three types of relative values of  $E^\ominus$  are of interest: (i) the difference in redox potentials between complexes  $ML_x^z$  and  $M'L_x^z$  of different metals in the same oxidation state and with the same coordination,  $\Delta(M, M') = E^\ominus(n, z) - E^\ominus(n+1, z)$  for two metals which are neighbours in the periodic system; (ii) the difference in redox potentials between two consecutive electron-transfer steps of the same complex;  $\Delta(\text{ox}, \text{red}) = E_{\text{ox}}^\ominus(n, z) - E_{\text{red}}^\ominus(n, z) = E^\ominus(n, z) - E^\ominus(n+1, z-1)$  (this has been previously called the redox stability [13] and represents the stability of a complex  $ML_x^z$  with respect to its disproportionation to  $ML_x^{z+1}$  and  $ML_x^{z-1}$ ); (iii) the difference in redox potentials between complexes  $ML_x^z$  and  $ML'_x{}^z$  of the same metal with a given oxidation state and coordination geometry but with different ligands,  $\Delta(L, L') = E^\ominus(ML_x^z) - E^\ominus(ML'_x{}^z)$ .

Values of  $E^\ominus$  are dominated by three contributions. The first of these, the energy of the redox electron in the reduced molecule, can for comparison of values of  $E^\ominus$  be conveniently replaced by the energy of the redox orbital including electron pairing energy when required,  $\epsilon(\text{redox})$ , according to Koopmans theorem. This contribution is our major concern here. Note that according to the IUPAC sign convention,  $+E^\ominus$  must be related to  $-\epsilon(\text{redox})$ . The second contribution, the free energy of solvation,  $\alpha^z$ , can be evaluated from the equation [16]:  $\alpha^z = -zF\chi - z^2S$ , in which  $F$  is the Faraday constant,  $\chi$  is the surface potential of the solution and  $S = Ne^2[1 - (1/D_s)]/2r$ , where  $N$  is Avogadro's number,  $D_s$  is the static dielectric constant of the solvent and  $r$  is the radius of the molecule. From this, it follows that the contribution of the solvation energy to  $\Delta(M, M')$  is nearly zero, i.e. solvation has a negligible effect on the redox potential difference between analogous complexes of different metals. The solvation energy contribution to  $\Delta(\text{ox}, \text{red})$  is  $-2S$ , i.e. solvation reduces the redox stability of any complex and there is a greater reduction for complexes smaller in size. The solvation energy contribution to  $\Delta(L, L')$  is a function of the charge on the ligands and of the radius of the molecules, hence its influence on redox potential differences of complexes of the same metal with different ligands varies. The third contribution arises from other physicochemical changes, e.g. changes in spin state and coordination environment. For a complex  $ML_x^z$ , the positions of the HOMO, corresponding to  $\epsilon(\text{redox})$  for the oxidation, and of the LUMO, corresponding to  $\epsilon(\text{redox})$  for the reduction, impose limits on the values of  $E_{\text{ox}}^\ominus$  and  $E_{\text{red}}^\ominus$  consequently, physicochemical changes are expected to lower  $E_{\text{ox}}^\ominus$ , raise  $E_{\text{red}}^\ominus$  and invariably decrease the redox stability,  $\Delta(\text{ox}, \text{red})$ , of such a complex. If the contribution due to physicochemical change is sufficiently large  $\Delta(\text{ox}, \text{red})$  may be reduced to zero or less and a transition involving two or more electrons may be observed.

### C. THE ENERGY OF THE REDOX ORBITAL

The energy of the redox orbital,  $\epsilon(\text{redox})$ , is written as a summation of two terms: (a) the energy of the lowest-lying  $d$  orbital, in  $O_h$  symmetry this is  $\epsilon(t_{2g})$ , and (b) the difference in energy between this orbital and the redox orbital; in  $O_h$  symmetry these values are zero,  $P$ ,  $\Delta_{\text{oct}}$  and  $P + \Delta_{\text{oct}}$ , depending on the  $t_{2g}e_g$  electron configuration where  $P$  denotes the electron pairing energy. Electron pairing energy is required whenever the redox orbital of the reduced species belongs to a more than half-filled subset.  $\Delta_{\text{oct}}$  is the octahedral ligand field splitting energy. The energy of the  $e_g$  orbital is written as  $\epsilon(e_g) = \epsilon(t_{2g}) + \Delta_{\text{oct}}$ .

Novel in this approach is the emphasis on the first term,  $\epsilon(t_{2g})$ , which in fact serves as a reference energy level permitting comparison between complexes of different metals, different valence states and/or different ligands. It is a very convenient reference since it is well defined in molecular orbital theory. Differences in  $\epsilon(t_{2g})$  contribute to differences in  $E^\circ$  values. A discussion of the origins of these differences,  $\Delta\epsilon(t_{2g})$ , is given below where it will be shown that  $\epsilon(t_{2g})$  is a reasonably smooth function of the number of  $d$  electrons,  $n$ , for a series of  $ML_x^z$  complexes with varying  $M$  and that  $\epsilon(t_{2g})$  also depends on  $L_x$  and on  $z$  [17].

#### (i) The influence of the metal

$\epsilon(\text{redox})$  is a step function of the number of  $d$  electrons,  $n$ , with steps for low-spin complexes of  $P$  at  $d^{3,4}$ , of  $\Delta_{\text{oct}} - P$  at  $d^{6,7}$  and of  $P$  at  $d^{8,9}$  and with steps for high-spin complexes of  $\Delta_{\text{oct}}$  at  $d^{3,4}$ , of  $P - \Delta_{\text{oct}}$  at  $d^{5,6}$  and of  $\Delta_{\text{oct}}$  at  $d^{8,9}$ . Plots of  $\epsilon(\text{redox})$  versus  $n$  for  $ML_x^z$  complexes with varying  $M$  are given in Fig. 1 for high-spin and in Fig. 2 for low-spin complexes, with an arbitrary slope for  $\epsilon(t_{2g})$  versus  $n$  and an arbitrary mean value for  $P$  and  $\Delta_{\text{oct}}$  in each figure. Certainly  $P$  and  $\Delta_{\text{oct}}$  vary irregularly for metal ions and ligand systems [9] within a series of complexes with the same ligand and so the use of a mean value is valid only to some approximation.

The experimental  $E^\circ$  values of the  $M(\text{H}_2\text{O})_6^{2+/3+}$  couples (Fig. 1) and the  $E_{1/2}$  values of the  $M(\text{dthc})_3^{0/+1}$  couples (Fig. 2) are also given. The experimental points for the two series of redox couples follow the model curves closely. The most striking observation is the large difference in slope,  $-\Delta\epsilon(t_{2g})/\Delta n$ , between the two series, it being approximately 1.5–1.9 V per  $d$  electron for the aquo complexes and 0.3–0.4 V per  $d$  electron for the dithiocarbamate complexes.

An interesting situation arises at the  $d^{5-7}$  interval of the low-spin with respect to the high-spin complexes: for low-spin complexes  $E_{\text{ox}}^\circ$  increases from  $d^5$  to  $d^6$  and decreases from  $d^6$  to  $d^7$ , but for high-spin complexes  $E_{\text{ox}}^\circ$

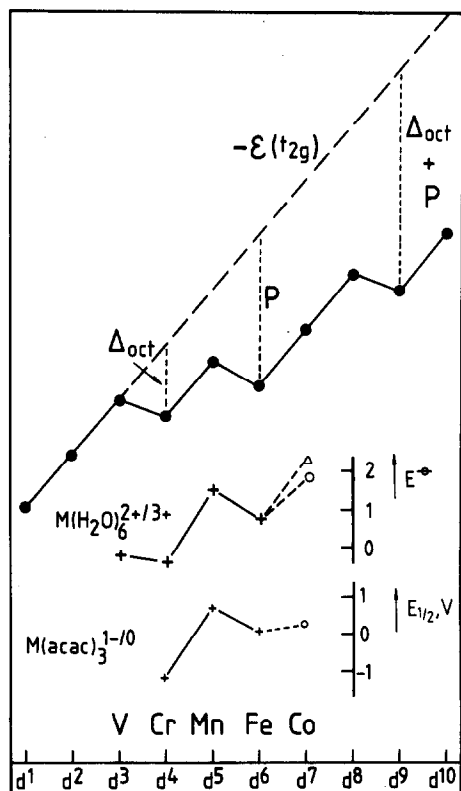


Fig. 1. Step function of  $E^\circ$  vs.  $d^n$  configuration for high-spin octahedral complexes;  $d^n$  and the model curve refer to  $M(II)$ . (●) Model points; (+ and ○) experimental; (○) influenced by physicochemical changes; (Δ) calculated for high-spin  $Co(III)$ .

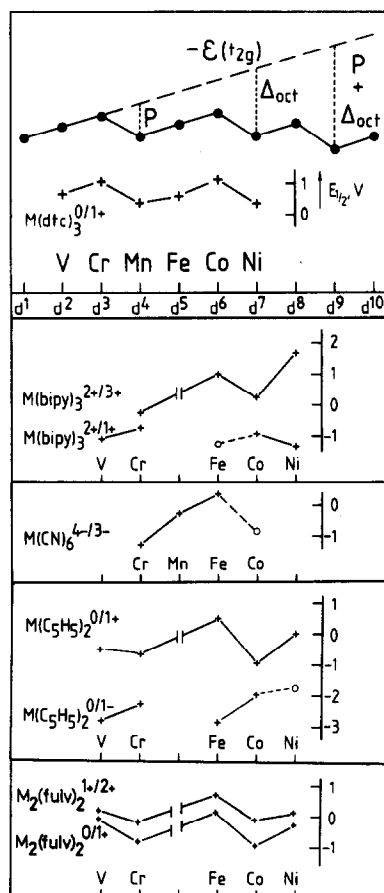


Fig. 2. Step function of  $E_{1/2}$  vs.  $d^n$  configuration for low-spin octahedral complexes;  $d^n$  and the model curve refer to  $M(III)$  for the dtc complexes and to  $M(II)$  for the other complexes. Symbols as in Fig. 1.

decreases from  $d^5$  to  $d^6$  and increases from  $d^6$  to  $d^7$ .

The complex  $Co(H_2O)_6^{3+}$  has a low-spin configuration. Due to the change of spin state the  $Co(H_2O)_6^{2+/3+}$  couple has a lowered  $E^\circ$ . This illustrates well the influence of a physicochemical change on  $E^\circ$ . Johnson and Sharpe [18] obtained a value of  $E^\circ = 2.6$  V for the high-spin form of  $Co(H_2O)_6^{3+}$  which is also given in Fig. 1.

Other series of complexes show similar dependencies of  $E_{1/2}$  on the

number of  $d$  electrons. Fig. 1 illustrates this dependency for high-spin  $M(\text{acac})_3$  and Fig. 2 for the low-spin  $M(\text{bipy})_3$  and  $M(\text{CN})_6$  complexes as well as for pseudo-octahedral  $M(\text{C}_5\text{H}_5)_2$ . The upper curves for each series of complexes in Fig. 2 correspond to the model curve; the lower curves will be discussed below. The series are less extensive than for the  $M(\text{dtc})_3$  complexes, but the trends are obvious. Once again, differences in the slope,  $-\Delta\epsilon(t_{2g})/\Delta n$ , are striking. Values for  $-\Delta\epsilon(t_{2g})/\Delta n$  based on the experimental curves from Figs. 1–3 are collected in Table 3.

Couples for which  $E^\circ$  may have been influenced by physicochemical changes are:  $\text{Co}(\text{acac})_3^{2+}/3+$ , lowered  $E^\circ$  due to a change of spin state;  $\text{Co}(\text{CN})_6^{3-}/\text{Co}(\text{CN})_6^{2-}$ , increased  $E^\circ$  due to a change of coordination environment;  $\text{Fe}(\text{bipy})_3^{2+}/1+$ , increased  $E^\circ$  due to a ligand centered redox transition.

Recently, electrochemical data on dinuclear metallofulvalene complexes,  $[\text{M}_2(\text{C}_{10}\text{H}_8)_2]^z$  ( $z = 0, 1+, 2+$ ), were reported [19]. For the two series of couples  $0/1+$  and  $1+/2+$  two similar curves for  $E_{1/2}$  versus  $n$  were found (Fig. 2). It can be shown that the doubling of energy levels in these dinuclear complexes causes a doubling of the curves of  $E_{1/2}$  versus  $n$  such that the  $[\text{M}_2(\text{C}_{10}\text{H}_8)_2]^{0/1+}$  and  $[\text{M}_2(\text{C}_{10}\text{H}_8)_2]^{1+/2+}$  oxidations both behave as if they were single  $M(\text{II})/M(\text{III})$  transitions. Such doubling does not imply that the redox electron is localised on one of the two metals.

### (ii) Redox stabilities

The contributions to  $\Delta(\text{ox, red})$  are  $-\Delta\epsilon(t_{2g})$  from the slope in  $\epsilon(t_{2g})$  and zero,  $P$ ,  $\Delta_{\text{oct}}$  or  $\pm(\Delta_{\text{oct}} - P)$  from the ligand field energy, in addition to

TABLE 3

Experimental magnitudes of  $\Delta(M, M')$ ,  $\Delta(\text{ox, red})$  and  $\Delta(L, L')$  for series of octahedral complexes

Ligand	$\Delta(M, M')$ , slope of $E^\circ$ vs. $n$	$\Delta(\text{ox, red})$ , slope of $E^\circ$ vs. $z$	$\Delta(L, L')$ <sup>b</sup> , slope of $E^\circ$ vs. $\Sigma\sigma^*$
$\text{H}_2\text{O}$	1.5–1.9	$\geq 2.0$	
$\text{R}_2\text{acac}^-$	1.5–1.9	$\geq 1.7$	$\sim 0.13$
$\text{CN}^-$	$\sim 0.8$		
$\text{RNC}^a$	$\sim 0.8$	0.5–0.9	
bipy	0.4–0.7	$\sim 0.7$	
$\text{C}_5\text{H}_5^-$	0.4–0.7	$\sim 0.7$	
$\text{R}_2\text{NCS}_2^-$	$\sim 0.35$	$\sim 0.9$	$\sim 0.09$
$\text{R}_2\text{C}_2\text{S}_2^{2-}$	$\sim 0.30$	$\sim 0.7$	$\sim 0.08$

<sup>a</sup> Data from ref. 25. <sup>b</sup>  $\sigma^*$  = Taft substituent constant.

$-2S$  from the solvation energy. This can readily be seen from Fig. 3 where the model curves for  $E_{\text{ox}}^{\circ}$  and  $E_{\text{red}}^{\circ}$  are given as a function of the number of  $d$  electrons for the low-spin case. Note that the lower curve, corresponding to  $E_{\text{red}}^{\circ}$ , is merely the upper curve, which corresponds to  $E_{\text{ox}}^{\circ}$ , shifted one unit of  $n$  to the left and to lower potential. In Fig. 3 the experimental  $E_{1/2,\text{ox}}$  and  $E_{1/2,\text{red}}$  values for a series of  $\text{M}(\text{dtc})_3$  complexes are also shown. There is a surprisingly good agreement between the model and experimental curves; the small and large redox stabilities coincide in the two cases.

Figure 3 shows why  $\text{Cr}(\text{dtc})_3$  and  $\text{Co}(\text{dtc})_3$  have a much larger redox stability than the other  $\text{M}(\text{dtc})_3$  complexes. It is obvious from the model that  $d^3$  and  $d^8$ , high-spin  $d^5$  and low-spin  $d^6$  octahedral complexes have a large redox stability, and that  $d^1$ ,  $d^2$ ,  $d^4$ ,  $d^7$  and  $d^9$  as well as low-spin  $d^5$  and high-spin  $d^6$  octahedral complexes have a small redox stability. Thus, this corresponds with the well-known stability of half-filled and filled subshell configurations. The reason for the stability of these configurations is either

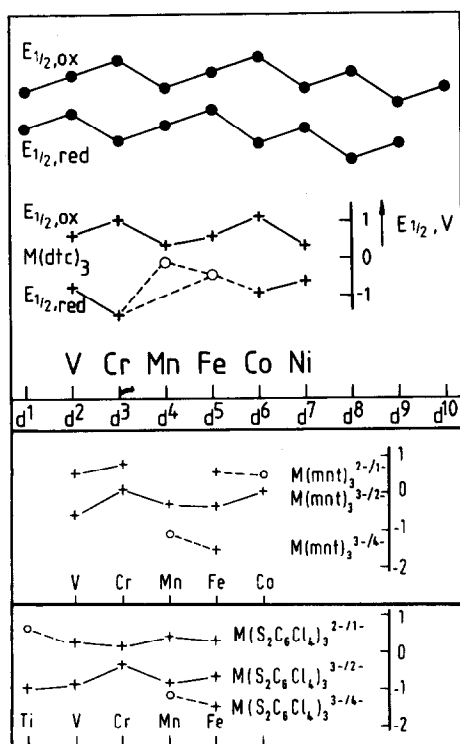


Fig. 3. Redox stability and  $d^n$  configuration for low-spin octahedral complexes;  $d^n$  and the model curves refer to  $\text{M}(\text{III})$ . Symbols as in Fig. 1.



the higher energy of the orbitals in the next subshell, or the electron pairing energy required to add electrons to the half-filled subshell.

The  $\text{Mn}(\text{dtc})_3^{0/1-}$  point deviates from the curve. In view of the position of the dtc ligand in the spectrochemical series, a high-spin configuration is expected for this complex, by analogy with the high-spin state of  $\text{Fe}(\text{II})(\text{dtc})_3^-$  [20] and in view of the high-spin/low-spin equilibrium of  $\text{Fe}(\text{III})(\text{dtc})_3$ . For  $\text{Fe}(\text{dtc})_3^{0/1-}$  a large influence of the spin state on  $E_{1/2}$  is not expected; the experimental  $E_{1/2}$  corresponds to  $t_{2g}^3 e_g^2 \rightarrow t_{2g}^4 e_g^2$ , with a  $d$  orbital contribution  $\epsilon(t_{2g}) - P$  about equal to the  $d$  orbital contribution from the  $t_{2g}^5 \rightarrow t_{2g}^6$  transition. For  $\text{Mn}(\text{dtc})_3^z$ , however, the transition  $t_{2g}^4 \rightarrow t_{2g}^3 e_g^2$  differs by  $2\Delta_{\text{oct}} - 2P$  from the  $t_{2g}^4 \rightarrow t_{2g}^5$  transition which may account for the deviation of the  $\text{Mn}(\text{dtc})_3^{0/1-}$  point from the curve.

In Fig. 3 are also given the  $E_{1/2}$  values of the first row complexes of some 1,2-dithiolates  $[\text{S}_2\text{C}_2(\text{CN})_2]^{2-}$  = maleonitriledithiolate, mnt, and  $\text{S}_2\text{C}_6\text{Cl}_4^{2-}$  = tetrachlorobenzene-1,2-dithiolate, tct]. According to Schrauzer [21], 1,2-dithiolates should be able to generate more extensive redox series than 1,1- and 1,3-dithiolates. He ascribes this to the charge rearrangement in the  $\pi$  system which is easier for the "even" 1,2-dithiolates than for the "odd" 1,1- and 1,3-dithiolates.

Close inspection of the  $E_{1/2}$  vs.  $n$  curves for the  $\text{M}(\text{III})(\text{mnt})_3^{3-/2-}$  couples and their tct analogues (Fig. 3) reveals some similarities with the dithiocarbamates, although the mnt and tct curves have smaller slopes,  $-\Delta\epsilon(t_{2g})/\Delta n$ , and lower redox stabilities. Compared with the metal dithiocarbamates, the redox potentials are much lower for the dithiolenes, about 1.1 V for mnt and 1.5 V for tct complexes. These lower  $E_{1/2}$  values may be a consequence of the larger donor strength of the dinegative 1,2-dithiolate ligands with respect to the mononegative 1,1-dithiolate ligand and imply that the +2 oxidation state of the metal can be achieved only for Mn(II) and Fe(II). For the other metals the +2 state lies below the potential range used experimentally. Furthermore, the  $\text{M}(\text{S}_2\text{C}_2\text{R}_2)_3^{2-/1-}$  redox couples become accessible for nearly all metals. For these oxidations the influence of the metal on the  $E_{1/2}$  vs.  $n$  plot has disappeared. The oxidation of the Ti(IV) complex with a  $d^0$  configuration is an indication that the redox orbitals are now ligand orbitals.

Couples which may have been affected by physicochemical changes are:  $\text{Co}(\text{mnt})_3^{2-}$ , lowered  $E_{1/2,\text{ox}}$  due to a two-electron transition and  $\text{Mn}(\text{S}_2\text{C}_2\text{R}_2)_3^{3-}$ , increased  $E_{1/2,\text{red}}$  probably connected with high-spin Mn(II), cf.  $\text{Mn}(\text{dtc})_3^-$ .

The dinuclear fulvalene complexes exhibit the completely different picture expected for two successive redox steps (Fig. 2); two parallel lines are found which indicate that similar ligand field contributions are present for both redox steps.

Once the contributions of  $\Delta_{\text{oct}}$  and  $P$  to the redox stability have been taken into account, the remaining contributions are  $-2S$  (due to the solvation energy) and  $-\Delta\epsilon(t_{2g})/\Delta z$ . For the dithiocarbamate complexes,  $-2S - \Delta\epsilon(t_{2g})/\Delta z$  is approximately 0.9 V. Fig. 2 shows that for the bipyridyl and cyclopentadienyl complexes this is about 0.7 V. The redox stabilities of the high-spin complexes are considerably greater than those of the low-spin complexes. Only limiting values of  $\Delta(\text{ox, red})$  can be given for the high-spin complexes since reduction of the M(II) aquo and acetylacetonato complexes usually results in metal deposition. The value of  $\Delta(\text{ox, red})$  exceeds 2.0 V for  $\text{M}(\text{H}_2\text{O})_6^{2+}$  and 1.7 V for  $\text{M}(\text{acac})_3^+$ . These data are summarized in Table 3.

The potential range spanned by an electron-transfer series is determined by the sum of the redox stabilities involved. The number of redox steps detected for such a series is limited by the potential range of the experiment. A large number of consecutive redox steps may be expected if  $-\Delta\epsilon(t_{2g})/\Delta z$  is small and if no large contribution due to a ligand field energy term ( $\Delta_{\text{oct}}$  or  $P$ ) is present. Only low-spin complexes have sufficiently low  $-\Delta\epsilon(t_{2g})/\Delta z$  values (see below) to exhibit extensive redox series. Therefore for octahedral complexes the larger electron-transfer series are expected for  $d^{0-3}$  and for low-spin  $d^{3-6}$ , in which cases a  $t_{2g}$  orbital set is filled from zero to three and from three to six electrons, respectively. Examples of these are:  $d^{0-3}$ ,  $\text{M}(\text{S}_2\text{C}_2\text{R}_2)_3^{0,1-,2-,3-}$  ( $\text{M} = \text{Cr, Mo, W}$ ) and  $\text{Re}(\text{S}_2\text{C}_2\text{R}_2)_3^{1+,0,1-,2-}$  [15];  $d^{3-6}$ ,  $\text{Fe}(\text{S}_2\text{C}_2\text{R}_2)_3^{1-,2-,3-,4-}$  [15],  $\text{M}(\text{dtc})_2[\text{S}_2\text{C}_2(\text{CN})_2]^{1+,0,1-,2-}$  ( $\text{M} = \text{Fe, Ru, Os}$ ) [22],  $\text{Os}(\text{dtc})_3^{2+,1+,0,1-}$  [23],  $\text{Cr}(\text{CN})_6^{3-,4-,5-,6-}$  [7] and  $\text{Cr}(\text{CNR})_6^{3+,2+,1+,0}$  [24].

### (iii) The influence of the ligand

For a discussion of the influence of the ligand on  $E^\circ$  values, the three relevant contributions are: (a) differences in solvation energy, a variable and therefore a complicated factor; (b) differences in  $\Delta_{\text{oct}}$  and in  $P$  (these differences are mostly negligible when only substituents on a ligand are varied but are especially relevant for very different ligands); (c) differences in  $\epsilon(t_{2g})$  which are related to the net donor strength of the ligand but also depend on the metal as can be seen from the large variation in slopes,  $\Delta\epsilon(t_{2g})/\Delta n$ , in Figs. 1–3. This implies that the ordering of  $E^\circ$  for  $\text{ML}_x^z$  complexes, even after correction for solvation energy and ligand field energy contributions, is not necessarily the same for each metal, nor is it necessarily equal to the ordering of the ligands L according to their net donor properties. In fact, the degree of covalency between metal and ligand must be taken into account as a second parameter. It has been argued that significant covalency should give rise to a large substituent effect on  $E_{1/2}$ , but

Nieuwpoort and Steggerda [26] have shown that this trend is not observed. Suggestions as to how covalency affects  $\epsilon(t_{2g})$  and the implications inter alia for the substituent effect on  $E_{1/2}$  are discussed in the next section.

#### D. THE $t_{2g}$ ENERGY LEVELS

In molecular orbital theory  $\epsilon(t_{2g})$  is described as the sum of the valence state ionisation energy (VSIE) of the  $d$  orbital of the metal  $M$  with effective charge  $q$ ,  $VSIE_M^q$ , and of a  $\pi$  covalency contribution,  $\Delta_\pi$ , thus  $\epsilon(t_{2g}) = -VSIE_M^q + \Delta_\pi$ . The VSIE is charge dependent. Usually this property is accounted for by the expression  $VSIE_M^q = \alpha_M + \beta_M q$ . For free ions,  $\beta$  is about 9–16 eV, however, due to covalency, the charge dependency is considerably reduced in complexes by a factor  $k$  ( $0 < k < 1$ ). Cotton and Harris [27] give a value of  $\Delta VSIE/\Delta q = k\beta_M = 1\text{--}5$  eV for chloro complexes of the heavier transition elements and Keijzers et al. [28] find that  $k\beta_M = 0.75\text{--}1.5$  eV for  $\text{Cu}(\text{dte})_2$ . Consequently,  $VSIE_M^q = \alpha_M + k\beta_M q$ .

Griffith [29] has shown that the experimental VSIE for free  $M(\text{III})$  ions, after correction for electron pairing, is a smooth function of the nuclear charge  $Z$ , and hence of the number of  $d$  electrons,  $n$ , increasing by about 80% from  $d^1$  to  $d^{10}$ . Hence VSIE may be expressed as a function of a reference value,  $VSIE_{\text{ref}}^q$ , thus  $VSIE_M^q = VSIE_{\text{ref}}^q(1 + \gamma n)$ , where  $\gamma$  is about 0.08. This relation is assumed to be valid for any charge  $q$ . Therefore as an approximate overall expression,  $VSIE_M^q = (\alpha_{\text{ref}} + k\beta_{\text{ref}} q)(1 + \gamma n)$ .

This formula is sufficiently sophisticated for a discussion of general trends. Equally useful for this purpose is the proportionality  $\Delta_\pi(\cdot)1/\Delta E_{\text{ML}}$ , from first-order perturbation theory.  $\Delta E_{\text{ML}} = E_M - E_L = -VSIE_M^q - E_L$  where  $E_L$  is the ligand orbital energy.  $\Delta_\pi$  is positive for a  $\pi$  donor ligand and negative for a  $\pi$  acceptor ligand. We are concerned with changes in  $\Delta_\pi$  and may write:  $d\Delta_\pi/dVSIE_M^q = d\Delta_\pi/dE_L = \Delta_\pi/\Delta E_{\text{ML}}$ . Hence,  $-d\epsilon(t_{2g})/dVSIE_M^q = 1 - \Delta_\pi/\Delta E_{\text{ML}}$ , which is denoted by  $A$ . This implies that changes in  $\epsilon(t_{2g})$  are smaller than changes in VSIE due to covalency. Furthermore, changes in charge  $z$  of the complex or changes in ligand donor strength affect  $q$  and thus  $VSIE_M^q$  since  $dVSIE_M^q/dq = k\beta_M$ . Consequently greater covalency implies a lesser change in  $\epsilon(t_{2g})$  with change in effective charge on the metal. Thus covalency reduction effects are superposed on changes in  $\epsilon(t_{2g})$ .

Contributions to  $\Delta(M, M')$  originate from  $d/dn$ , which operates on  $VSIE_M^q$  while contributions to  $\Delta(\text{ox}, \text{red})$  come from  $d/dz$  operating on  $q$ . Contributions to  $\Delta(L, L')$  are due to changes in ligand orbital parameters, represented by  $d/d\psi_L$ . One part of  $d/d\psi_L$  is  $\partial/\partial E_L$ ,  $d/d\psi_L$  operates on  $q$  and  $\partial/\partial E_L$  operates on  $\Delta_\pi$ . This results in

$$\Delta(M, M'): -d\epsilon(t_{2g})/dn = A\gamma(\alpha_{\text{ref}} + k\beta_{\text{ref}} q) \quad (1)$$

$$\Delta(\text{ox, red}): -d\epsilon(t_{2g})/dz = Ak\beta_M(dq/dz) \quad (2)$$

$$\Delta(L, L'): -d\epsilon(t_{2g})/d\psi_L = Ak\beta_M(dq/d\psi_L) - \Delta_\pi/\Delta E_{ML} \quad (3)$$

where  $A = 1 - \Delta_\pi/\Delta E_{ML}$ . The following parameters have therefore to be considered when discussing trends in redox potentials:  $q$ ,  $dq/dz$ ,  $dq/d\psi_L$ ,  $k$ ,  $\Delta_\pi/\Delta E_{ML}$  and, eventually,  $\gamma$ . From these parameters  $dq/dz$  and  $dq/d\psi_L$  are determined (i) by the extent of metal character in the redox orbital and (ii) by the ease of charge redistribution in the complex. Both (i) and (ii) are related to the covalency of the metal–ligand bond;  $k$  and  $\Delta_\pi/\Delta E_{ML}$  also depend on this covalency, whereas  $q$  depends on the net ( $\sigma + \pi$ ) donor strength of the ligands and the formal oxidation state of the metal. Hence, trends in redox potentials can be discussed in a chemical way by considering how changes in the net donor strength and in the extent of covalency affect the six parameters. This is presented in Table 4. Contributions from the solvation energy are included but  $\gamma$  has not been considered. The value of  $\gamma$  presumably decreases with the effective metal charge  $q$ .

The trends presented in Table 4 are in direct agreement with the experimental results collected in Table 3. With regard to the slopes related to  $\Delta(M, M')$ , a better understanding of the quantitative values can be obtained from eqn. (1). Experimentally, the slopes occur in the range 0.3–1.9 V per  $d$  electron. With values of  $A$  between 0.5 and 1.0, of  $\alpha_{\text{ref}} + k\beta_{\text{ref}}q$  between 8 and 24 eV and  $\gamma \lesssim 0.08$ , the entire experimental range can be covered. Neither  $A$  nor  $k$  alone can cause such a large range but together they can.

According to eqn. (2) the redox stabilities depend on  $dq/dz$ , which approximately represents the extent of metal character of the redox orbital. The covalency reduction factor  $k$  also enters into the equation which implies that the redox stability is enhanced by differences in the amount of metal

TABLE 4

Survey of trends

	As donor strength increases	As covalency increases				As radius increases
	$q$ decreases	$dq/dz$ decreases	$dq/d\psi_L$ increases	$\Delta_\pi/\Delta E_{ML}$ increases	$k$ decreases	$S$ decreases
$\Delta(M, M')$	decreases			decreases	decreases	
$\Delta(\text{ox, red})$		decreases		decreases	decreases	increases
$\Delta(L, L')$			increases	decreases	decreases	

character. With values of  $A$  between 0.5 and 1.0, of  $k\beta_M$  between 0.75 and 5 eV and of  $dq/dz$  between 0.5 and 1.0 (at least 50% metal character) the entire experimental range of  $\Delta(\text{ox, red})$ , 0.3–2.0 V, can be covered.

Concerning the influence of ligand substituents, the model indicates that there are opposing contributions to  $\Delta(L, L')$ . The experimental data reveal that ligand substituent effects decrease with increasing covalency. Hence in cases of significant covalency the lowering of the charge dependency of the VSIE and other contributions to  $\Delta\epsilon(t_{2g})$  outweigh the increase due to the increased ligand character of the redox orbital.

In conclusion, the model presented here provides an improved understanding of many experimental electrochemical data in both a qualitative and semiquantitative way. Its emphasis on the  $t_{2g}$  energy level may be unrealistic when an  $e_g$  level is involved, but if necessary the model can be adapted. As far as has been checked, the model is equally valid for second and third row transition metals, but owing to the increased tendency to conform to the 18-electron rule, no long series of octahedral metal complexes are found there. Finally, electrochemical data of complexes which have other geometries (notably square planar) fit the basic characteristics of the model with contributions from the position of the lowest-lying  $d$  orbital, the ligand field splitting energy and the spin pairing energy.

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