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ELECTROCHEMICAL INVESTIGATION OF COORDINATION COMPOUNDS

II*. PHOSPHINE DERIVATIVES OF Co^0 AND Ni^0. CORRELATIONS BETWEEN $E_{1/2}$, ΔHNP AND ν(CO) IN THESE COMPLEXES

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Summary

The complexes $[Co(CO)_3L]_2$, $Hg[Co(CO)_3L]_2$, $HgCo_2(CO)_{8-n}L_n$ and $Ni(CO)_{4-n}L_n$ ($L = PR_3$, $P(OR)_3$) have been reduced electrochemically. The $E_{1/2}$ values of the reduction processes are dependent on L and *n*. These values can be related to the ΔHNP values of the ligands and to the CO stretching frequency of the molecules. The results can be interpreted in terms of either kinetic or thermodynamic factors.

Introduction

In a previous paper [1] we described the oxidation—reduction mechanism for Co^I, Rh^I, Ir^I systems obtained by the reactions of phosphorus ligands with $[Co(CO)_4]_2$, $[RhCl(CO)_2]_2$ and $[Ir(CO)_3Cl]_n$. We noted that in the case of $RhCl(CO)L_2$ complexes the $E_{1/2}$ values could be correlated to the basicity of the ligand L. This suggested that the electrode process could be used as a tool to investigate electron transfer in any organometallic carbonyl compounds in relation to the shift of the CO stretching frequency.

We now report a similar study of the complexes $[Co(CO)_4]_2$, $Hg[Co(CO)_4]_2$, $Ni(CO)_4$ and some of their phosphine derivatives of formula $[Co(CO)_3L]_2$, $Hg[Co(CO)_3L]_2$, $Ni(CO)_{4-n}L_n$ with $L = PR_3$, $P(OR)_3$. In theory, by replacing one or more of the carbonyl groups by other ligands L in organometallic carbonyl compounds, one can determine some properties of these ligands as well as the bonding schemes of the metal carbonyl moiety by studying the change of the carbonyl stretching frequencies as a function of the ligand L [2,3].

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* For part I see ref. 1.

Experimental

Apparatus

The polarographic and controlled potential electrolysis apparatus has been described previously [1].

Chemicals

Tetrahydrofuran (Prolabo, technical grade) was purified by distillation from $LiAlH_4$ under nitrogen, vapour transferred into a solvent vessel which contained Na/K alloy (1/1 by weight), then vapour transferred into the electrochemical cell.

Tetrabutylammonium perchlorate (TBAP) was prepared from the metathetical reaction between perchloric acid and tetrabutylammonium hydroxid (Fluka, 40% in water) and recrystallized twice from THF.

The compounds used were available in this laboratory or were synthesized and purified by published methods [4]. Polarographic measurements were carried out using a dropping mercury electrode ($m^{2/3}\ t^{1/6} = 1.80$ at 0 V) as cathode, a Pt wire as anode, and Ag/Ag^I ($AgClO_4$ 10^{-3} M, Bu_4NClO_4 10^{-1} M) as reference electrode. Unless otherwise stated all solutions for electrochemical studies were 10^{-3} M.

Results and discussion

Correlation between the $E_{1/2}$ values and the ligand basicity

Non-aqueous titrimetry has proved fruitful for determining the relative basicities of water insoluble compounds. The correlation between pK_a (H_2O) and $E_{1/2}$ or ΔHNP for a particular non-aqueous solvent has been demonstrated by several authors [5], and the relative basicities of a group of compounds can be established for a particular solvent through the use of $E_{1/2}$ or ΔHNP (half neutralization potential) values. The basicities of various substituted phosphines were measured in this way by Streuli [6] (Table 1).

Paliani et al. [7] recently studied some phosphine derivatives of π-allyl-

TABLE 1

ΔHNP OF THE PHOSPHINE LIGANDS L AND $E_{1/2}$ VALUES FOR THE $[Co(CO)_3L]_2$ AND $Hg[Co(CO)_3L]_2$ COMPLEXES

Ligand L	ΔHNP[a]	$[Co(CO)_3L]_2$ $-E_{1/2}$	$Hg[Co(CO)_3L]_2$ $-E_{1/2}$
CO		0.75	0.96
$P(OPh)_3$	875	0.90	1.08
PPh_3 (2)	573	1.30	1.62
$P(OEt)_3$	420	1.47	1.72
PMe_2Ph	281	1.70	1.93
PMe_3	114	1.92	2.21
PEt_3	111	1.86	2.18

[a] ΔHNP indicates the semi-neutralisation potentials, referred to that of *N,N'*-diphenylguanidine as standard, in nitromethane as solvent [6]. [b] 10^{-4} M solution.

tricarbonylcobalt π-$C_3H_5Co(CO)_3$. For the complexes π-$C_3H_5Co(CO)_2L$ the plot of half-wave potential against ΔHNP is a straight line.

In our present study other cobalt complexes ($[Co(CO)_3L]_2$ and $Hg[Co(CO)_3L]_2$) were investigated (Table 1). At 25°C the electrochemical reduction at the dropping mercury electrode (DME) of $[Co(CO)_3L]_2$ and $Hg[Co(CO)_3L]_2$ in THF containing TBAP (10^{-1} *M*) occurs in a two-electron step, as the homodimetallic parent analog $[Co(CO)_4]_2$ and $Hg[Co(CO)_4]_2$. The limiting current is consistent with a two-electron reduction (as ascertained by controlled potential electrolysis), and the wave height varies as the square root of the head of the DME indicating a diffusion-controlled process. The theoretical equation of the curve $\log i/i_d - i = f(E)$ established for reversibility of the system is not verified. From these results eqns. 1 and 2 can be proposed for the reduction of these compounds:

$$[Co(CO)_3L]_2 + 2e \rightarrow 2\,Co(CO)_3L^- \quad (1)$$

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

The plot of $E_{1/2}$ of these compounds against ΔHNP of the phosphine ligands L is shown in Fig. 1: a linear variation is observed. It can be concluded that the half-wave potential is predominantly influenced by the capacity of the ligand to transfer σ electrons to the metal ions. An increase of electron density on the metal atom (*s*) would then shift $E_{1/2}$ towards more negative value.

Correlation between the $E_{1/2}$ values and the ν(CO) (totally symmetrical mode)

Kinetics of the electron transfer

Vlcek [8] has previously shown the existence of correlations between the polarographic behaviour of coordination compounds and their electronic struc-

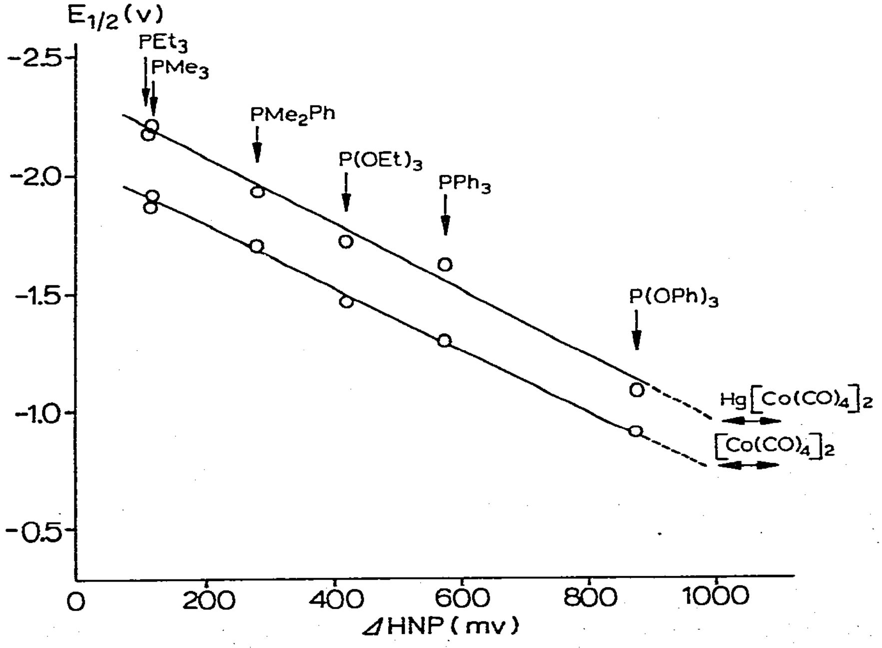


Fig. 1. $E_{1/2}$ of the $[Co(CO)_3L]_2$ and $Hg[Co(CO)_3L]_2$ complexes vs. ΔHNP of the phosphine ligand L.

ture. Recently, an extended study of the electrochemical reduction-scission of compounds containing metal—metal bonds indicated that a possible parallel exists between the reduction potential and the bond strength [9]. More recently, Piro [10] has extended the theories of Marcus [11] and Levich [12] to the main factors influencing the kinetics of the electron transfer. In electrokinetics, the factors Λ (the rate constant of the whole process during which the electron change takes place) and α (the transfer coefficient) are closely related to a kinetical factor λ of reorganisation of internal (λ_i) and external (λ_e) coordination spheres of the ion under consideration.

$$\lambda = \lambda_i + \lambda_e \tag{3}$$

The most characteristic term, λ_i, depends on the structure of the complex:

$$\lambda_i = \frac{1}{2} \sum{}_{jK} K_{jK} \Delta q_j \Delta q_K \tag{4}$$

where K_{jK} is reduced force constant and Δq the difference between the coordinates of the bond in the reduced and oxidized products. Basolo and Pearson [13] postulate that this last term depends essentially on the variations of the coordinates. Furthermore, for the similar complexes characterized by λ_1 and λ_2 Piro has proposed that the difference between the $E_{1/2}$ values of these complexes is:

$$\Delta E_{1/2} = \frac{\lambda_1 - \lambda_2}{2nF} \tag{5}$$

In our case, let us consider the variation of the potential energy λ_i in a model complex L—M—CO as a simplified pattern for the studied compounds (with M including the central metal atom and the other ligands).

Eqn. 4 can be simplified by noting that K_{CO} is the most important force constant. So:

$$\lambda_i \simeq \tfrac{1}{2} K_{CO} (\Delta q_{CO})^2 \tag{6}$$

In a series of analogous complexes, the variation $\Delta\lambda_i$ will become:

$$\Delta\lambda_i \simeq \Delta[K_{CO}(\Delta q_{CO})^2] \tag{7}$$

and if we suppose that the variation of the normal coordinates does not really change along a series of similar complexes:

$$\Delta\lambda_i \simeq \mathrm{ct} \times \Delta K_{CO} \tag{8}$$

Furthermore, taking into account the relation between the force constant and the CO stretching frequency ν(CO)

$$\Delta\lambda_i \simeq \mathrm{ct} \times [\nu(\mathrm{CO})]^2 \tag{9}$$

From eqns. 5, 8 and 9, it can be deduced that, along a series of similar complexes (such as $[Co(CO)_3L]_2$ or $Hg[Co(CO)_3]_2$), the variation $\Delta E_{1/2}$ of the half-wave potential between two complexes is adequately represented by

$$\Delta E_{1/2} = (\mathrm{ct})' \times \Delta[\nu(\mathrm{CO})]^2 \tag{10}$$

Because of the considered approximations, the mathematical form of this equation cannot be regarded as very significant, but it is our opinion that the exis-

TABLE 2

INFRARED CO STRETCHING FREQUENCIES AND $E_{1/2}$ VALUES FOR THE COMPLEXES $[Co(CO)_3L]_2$, $Hg[Co(CO)_3L]_2$

Ligand L	$[Co(CO)_3L]_2$		$Hg[Co(CO)_3L]_2$	
	$\nu(CO)^a$	$-E_{1/2}$	$\nu(CO)^a$	$-E_{1/2}$
PEt_3	1972	1.86	1987	2.18
PMe_3	1970	1.92	1987	2.21
PMe_2Ph	1975	1.70	1990	1.93
$PMePh_2$	1976	1.53	1990	1.80
PPh_3	1977	1.30^b	1991	1.62^b
$P(OEt)_3$	1992	1.47	—	1.72
$P(OMe)_3$	1995	1.30	2005	1.50
$Ph_2P(OMe)$	1982	1.33	1996	1.55
$PhP(OMe)_2$	1987	1.30	2001	1.55
$P(OPh)_3$	1998	0.90	—	1.08

[a] In hexadecane solution. [b] 10^{-4} *M* in THF—TBAP solutions.

tence of an experimental relation between $E_{1/2}$ and ν(CO) has a fundamental basis.

In the particular case of complexes $[Co(CO)_3L]_2$ and $Hg[Co(CO)_3L]_2$ with different ligands L (Table 2), and $Ni(CO)_{4-n}[P(OMe)_3]_n$ and $Hg\{Co_2(CO)_{8-n}[P(OMe)_3]_n\}$ with *n* variable (Table 3) the plots of $E_{1/2}$ against ν(CO), in agreement with eqn. 10, appear as parabolic curves (Figs. 2—5).

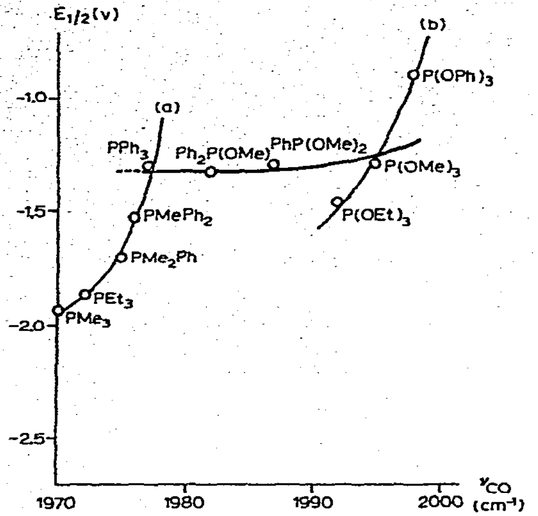
In Fig. 3, the compounds $Hg[Co(CO)_3P(OPh)_3]_2$ and $Hg[Co(CO)_3P(OEt)_3]_2$ have a different symmetry [14] and thus are not strictly comparable. For the same reasons the Co^0 complexes $Co_2(CO)_{8-n}L_n$ (with *n* variable) cannot be compared (bridged or non-bridged structures). The complexes $Hg[Co(P(OMe)_3)_4]_2$ and $Ni[P(OMe)_3]_4$ are not reduced up to —4 V (vs. $Ag/AgClO_4$ 10^{-1} *M*). At 25°C the electrochemical reduction at the dropping mercury electrode of $Ni(CO)_{4-n}L_n$ complexes in THF containing TBAP (10^{-1} *M*) occurs in a one-elec-

TABLE 3

INFRARED CO STRETCHING FREQUENCIES AND $E_{1/2}$ VALUES FOR THE COMPLEXES $Hg\{Co_2(CO)_{8-n}[P(OMe)_3]_n\}$ AND $Ni(CO)_{4-n}[P(OMe)_3]_n$

Compounds	$\nu(CO)^a$	$-E_{1/2}$
$Hg\{Co_2(CO)_{8-n}[P(OMe)_3]_n\}$		
$n = 0$	2070^b	0.96
$n = 2$	1995^b	1.50
$n = 4$	1935^b	2.20
$n = 6$	1875^b	3.12
$Ni(CO)_{4-n}[P(OMe)_3]_n$		
$n = 0$	2125^c	2.80
$n = 1$	2070	2.95
$n = 2$	2024	3.30
$n = 3$	1963	3.90 (?)

[a] In hexadecane solution. [b] In CsBr pellets. [c] Raman spectrum.



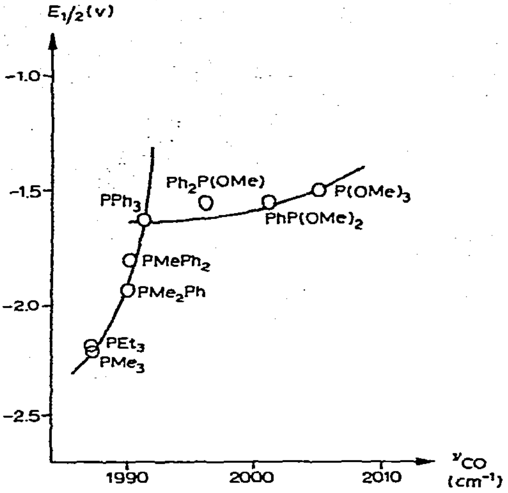


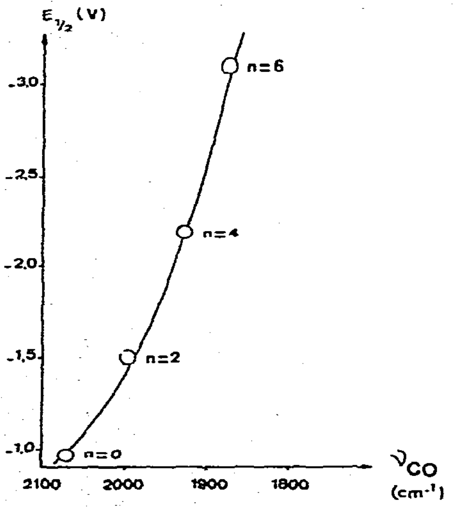
Fig. 2. $E_{1/2}$ vs. ν(CO) (totally symmetrical mode) of the $[Co(CO)_3L]_2$ complexes.

Fig. 3. $E_{1/2}$ vs. ν(CO) (totally symmetrical mode) of the $Hg[Co(CO)_3L]_2$ complexes.

tron step. The theoretical equation of the curve $\log i/i_d - i = f(E)$ established for reversibility of the system is not verified.

Thermodynamic interpretation

Infrared spectroscopy indicates the variations (importance and direction) of the electronic charge on the central metal atom. In particular, it is known that a decrease of the CO stretching frequency indicates an increase of the charge. Thus



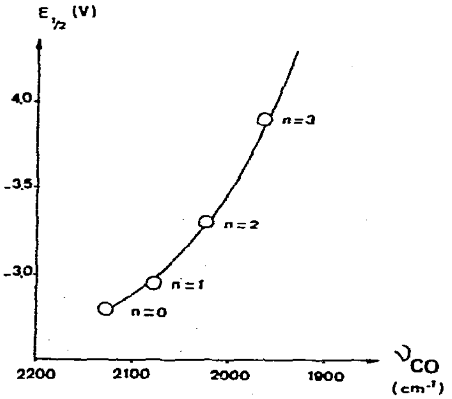


Fig. 4. $E_{1/2}$ vs. ν(CO) (totally symmetrical mode) of the $Hg[Co_2(CO)_{8-n}L_n]$ complexes.

Fig. 5. $E_{1/2}$ vs. ν(CO) (totally symmetrical mode) of the $Ni(CO)_{4-n}L_n$ complexes ($L = P(OMe)_3$).

the possibility cannot be excluded that the relation between $E_{1/2}$ and ν(CO) has a thermodynamic basis. More explicitly, in terms of the definition of $E_{1/2}$, its variations with the ligand L (or with the degree of substitution n) could also be due to the E_0* variations.

From this point of view, the relatively small value of the half-wave potential for $[Co(CO)_4]_2$ and $Hg[Co(CO)_4]_2$ indicates that the electron transfer takes place to an orbital of relatively high electronic affinity. Entry of two electrons into this orbital involves a modification in the electronic structure of the starting material. It can be suggested that in $Hg[Co(CO)_4]_2$ there is a small degree of polarization of the metal—metal bond in the sense $Hg^{+\delta}—Co^{-\delta}$. Therefore, as $Hg[Co(CO)_4]_2$ is reduced at a lower potential than $[Co(CO)_4]_2$, the first orbital used is probably localised on the cobalt atom. If the orbital were localised on the mercury atom, $Hg[Co(CO)_4]_2$ would be reduced at more positive potential than $[Co(CO)_4]_2$. The same pattern was observed with the substituted complexes $[Co(CO)_3L]_2$ and $Hg[Co(CO)_3L]_2$.

Figs. 2 and 3 show that the energy required to reduce $[Co(CO)_3L]_2$ and $Hg[Co(CO)_3L]_2$ complexes is a function of the ligand basicity. Increasing basicity of the ligand L increases the electronic density of the whole molecule, an extra-electron will be accepted with more difficulty and the complex will be reduced at more negative potential.

Figs. 4 and 5 show that increasing the substitution increases the electronic density on the orbitals of the metal atom. This leads, on the one hand, to a shift of the CO stretching frequency to lower values, and on the other hand to reduction of the complexes at more negative potentials. The higher the value of n, the more difficult it is to reduce the complex; therefore $Ni[P(OMe)_3]_4$ (Fig. 5) cannot be reduced before reduction of the solvent (or electrolyte).

In Fig. 2, the plot of half-wave potential against the CO stretching frequency for the $[Co(CO)_3L]_2$ complexes reveals a difference in behaviour in between complexes containing ligand phosphines and phosphites. This behaviour shows that at least two types of structural parameters control the variations of $E_{1/2}$ and ν(CO) each of them having a more specific relation to one of these experimental values. It is tempting to suppose that the energy of the useable unoccupied orbital $E_{1/2}$ is more directly connected with the σ donor ability of the ligand, whereas the ν(CO) frequency depends on the difference between σ donor and π acceptor ability of the ligands.

The distance between the curves (a) to (b) could be a measure of the greater electron π acceptor ability of phosphites compared to phosphines.

As far as the localisation of the unoccupied orbital under investigation in the $[Co(CO)_3L]_2$ complexes is concerned, there are three possibilities:

(*i*) localisation on the metal atom, which would give a reduction potential value near to that of $[Co(CO)_4]_2$.

(*ii*) localisation on the ligand L, which would give a value near to that of L (for $P(OMe)_3$: $E_{1/2} = -3.30$ V; for PPh_3: $E_{1/2} = -3.50$ V).

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* In the case of $[Co(CO)_4]_2$, the normal potential E_0 has been measured. From the Nernst's equation $E = E_0 + 0.058/n \log [ox]/[red]$, with variable concentrations of $[ox] = [Co_2(CO)_8]$ and constant concentration of $[red] = [Co(CO)_4^-]$, E_0 was equal to —0.65 V (in THF containing TBAP (10^{-1} *M*), Ag/Ag^I as reference electrode). For the couple $[Co(CO)_3L]_2/[Co(CO)_3L^-]$ the E_0 value has not been measured.

(*iii*) intermediate localisation which would give intermediate values. It is this third possibility which seems to apply in the present study, as in other cases [15].

We must emphasize that the validity of the reasoning above is probably limited to carbonyl complexes, and that the uncertainty in our interpretation in terms of either kinetic or thermodynamic factors calls for further investigation.

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References

1 D. de Montauzon and R. Poilblanc, J. Organometal. Chem., 93 (1975) 397.
2 F.A. Cotton, Inorg. Chem., 3 (1964) 702.
3 R.J. Angelici and M.D. Malone, Inorg. Chem., 6 (1967) 1731.
4 A. Sacco, Ann. Chim., 43 (1953) 495; W. Hieber and W. Freyer, Chem. Ber., 91 (1960) 492; C. Pegot, Thèse 3ème cycle, Toulouse (1969); D. de Montauzon and R. Poilblanc, J. Organometal. Chem., 54 (1973) 291; J. Newman and A.R. Manning, J. Chem. Soc. Dalton Trans., 2 (1972) 241; M. Bigorgne, Bull. Soc. Chim., (1960) 1986.
5 H.K. Hall, J. Phys. Chem., 60 (1956) 60; C.A. Streuli, Anal. Chem., 31 (1959) 1652.
6 C.A. Streuli, Anal. Chem., 32 (1960) 985.
7 G. Cardaci, S.M. Murgia and G. Paliani, J. Organometal. Chem., 77 (1974) 253.
8 A.A. Vlcek, in Progress in Inorganic Chemistry, (F.A. Cotton Ed.) Vol. 5, Interscience, London, 1963.
9 R.E. Dessy, P.M. Weissman, J. Amer. Chem. Soc., 88 (1966) 5124 and references therein.
10 J. Piro, J. Chim. Phys., 68 (1971) 1368.
11 R.A. Marcus, J. Chem. Phys., 43 (1965) 679.
12 V.G. Levich and R.R. Dogonadze, Int. Comm. Electrochem. Thermodyn. Kinet. 14th Meeting, Moscow, 1963.
13 E. Basolo and R.G. Pearson, Mechanisms of Inorganic Reactions, 2nd edn., John Wiley, New York, 1958.
14 J. Newman and A.R. Manning, J. Chem. Soc. Dalton Trans., (1972) 241.
15 A.A. Vlcek, Electrochim. Acta, 13 (1968) 1063.