Metal-Localized Protonation of $Mmnt_2^{3-}$ (M = Rh, Co) Complexes

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The reaction of electrochemically generated $Mmnt_2^{3-}$ (M = Rh, Co, Ni) complexes with weak protonic acids was studied using various electrochemical techniques. Complexes with M = Rh and Co react under the formation of a protonated species from which hydrogen is evolved at a dropping mercury electrode at potentials more negative than are those of the $Mmnt_2^{2-}/Mmnt_2^{3-}$ couple. Comparison with the behaviour of other protonated transition metal complexes led to the conclusion that the protonation site in $Mmnt_2^{3-}$ units is the metal atom. Protonation of $Rhmnt_3^{3-}$, prepared by reduction with $LiAlH_4$, was studied spectrophotometrically in solution. $[Rh(H)-mnt_2]^{2-}$ gives a characteristic band at 464 nm. Reduction of the latter species leads to $Rhmnt_2^{3-}$ whereas oxidation results in $Rhmnt_2^{2-}$. $[Rh(H)-mnt_2]^{2-}$ decomposes slowly in solution under the formation of $Rhmnt_2^{2-}$ and hydrogen evolution; the stability of the corresponding Co-species is considerably smaller. $Nimnt_2^{3-}$ is oxidized rapidly by the weak acids used to give $Nimnt_2^{2-}$.

Introduction

Recently, we have analyzed the capability of planar complexes for the substrate addition, using simple perturbation theory [1]. From these considerations it follows that redox addition to central metal atom is energetically unfavourable in complexes with extensive mixing of metal and ligand out-of-plane π-orbitals. This is due to the loss of delocalization energy which would arise in the oxidized state and which could hardly be compensated for by the energy of the newly formed axial bond. However, simple σ-addition of Lewis acids to the sufficiently basic metal center has been predicted not to be so strictly restricted.

To test these predictions experimentally, we followed the interaction of $Mmnt_2^{3-}$ (M = Rh, Co, Ni, mnt = maleonitriledithiolate = $S_2C_2(CN)_2^{2-}$) with weak protonic acids. Bis dithiolate complexes are known to have an extensively delocalized ground state [2, 8]. The trianions $Mmnt_2^{3-}$ were found

recently to be formed by electrochemical as well as chemical reduction of corresponding dianions [3–7]. All experimental data point to the conclusion that metal atoms in these trianions are formally in the oxidation state (I) [3–7] and can thus be expected to be strongly basic. From all $Mmnt_2$-trianions observed, $Rhmnt_2^{3-}$ seems to have the highest basicity of n-type, as the highest occupied orbital is the metal-localized d_{z^2} orbital [22].

Weak protonic acids were chosen as carriers of strong Lewis acid, H^+, which can be transferred to the basic site in the complex. However, oxidation or redox addition could also be expected in interaction with strongly reducing, coordinatively unsaturated substrates.

Experimental

Chemicals

$Na_2mnt = Na_2S_2C_2(CN)_2$ was prepared according to [12]. $Rh_2(CH_3COO)_4 \cdot 2CH_3OH$ was synthetized according to [13].

As solutions of $Rhmnt_2^{2-}$ are very air-sensitive, all synthetic procedures described below were performed in pure argon atmosphere in the Schlenk-type apparatus. All solvents were oxygen free and handled only in closed apparatus.

$[Bu_4N]_2[Rhmnt_2]$ was prepared by modified procedure described in [14]: 0.5 g of solid Rh_2-$(CH_3COO)_4 \cdot 2CH_3OH$ was added under pure argon atmosphere to the solution of 0.740 g of Na_2mnt in 8 ml of absolute methanol. The colour of the solution immediately turned dark green. After 40 minutes of stirring, 8 ml of the methanolic solution of $[Bu_4N]$-OH (prepared from 5 g Bu_4NCl and methanolic suspension of Ag_2O) was added. Very dark solid precipitated from this mixture at 0 °C during 20 minutes. This material was filtered-off, washed with isopropyl alcohol, dissolved in 50 ml of acetone, filtrated and 20 ml of isopropyl alcohol were added. Acetone was then distilled off. Resulting solution was cooled to −20 °C. Dark microcrystalline solid crystallized from this solution during 1 hr. This solid

product was filtered off, washed several times with isopropyl alcohol and finally with pentane and dried under *vacuum*. The product was spectrally and by the analysis characterized as [Bu$_4$N]$_2$[Rhmnt$_2$]. The yield was 0.46 g, *i.e.* 27% based on Rh$_2$(CH$_3$COO)$_4$· 2CH$_3$OH. Solid product is air-stable, but its solutions are readily oxidized by air to dark brown-red solutions.

[Bu$_4$N]$_2$[Comnt$_2$] and [Bu$_4$N]$_2$[Nimnt$_2$] were prepared according to [15]. Bu$_4$NPF$_6$ (Ozark–Mahoning Co.) was dried under vacuum for 24 hours at 100 °C.

Tetrahydrofuran (THF) (Merck) was purified by the ketyl method [16].

Instrumentation

Polarographic measurements were performed on LP-7e polarograph (Laboratorní přístroje, Prague, Czechoslovakia) with potentiostat modified according to LP-9 polarograph. Polarograms were recorded on the LP 4103 XY recorder. Potential values were measured against saturated calomel electrode (SCE).

Kalousek commutator measurements [18, 19] were performed using an instrument with a synchronous mercury drop-time to provide a constant number (M) of rectangular potential pulses layed on each mercury drop. This instrument acts at the same time as a potentiostat, so that both generation potential and measuring potential are compensated for the iR drop. In all measurements 18 pulses (M) at one mercury drop with frequency f = 12.5 Hz were used, *i.e.* the drop time was 1.44 s (M = f·t). For M = 18, it follows from the theoretical equations [18] that the value of the ratio of commutated to diffusion current, $(\bar{i}_c/\bar{i}_d)$, in the absence of adsorption and kinetic phenomena, equals 2.356. The value of $\bar{i}_c/\bar{i}_d$ is a measure of the amount of the product of electrode reaction at the electrode surface. Decrease of this ratio below this theoretical value indicates a follow-up reaction of the primary product of the electrode reaction [18]. The magnitude of this decrease is a measure of the extent of the follow-up reaction. The value $\bar{i}_c/\bar{i}_d$ = 0.5 is the lowest theoretical limit, *i.e.* this value corresponds to the situation when no primary product of the electrode reaction is present at the electrode surface.

Cyclic voltammetry measurements were performed using the sweep generator and potentiostat [17]. Uncompensated iR drop was eliminated by means of the additional positive feedback circuit. Cyclic voltammograms were measured by single potential sweep on dropping mercury electrode (DME). The sweeps started 3.1 s after the beginning of the drop. Curves were recorded on the Tektronix 5103 N oscilloscope.

The vacuable polarographic cell was used for electrochemical measurements. The reference electrode was separated from the depolarizer solution by the

frit-tube containing the THF solution of Bu$_4$NPF$_6$. Pt-wire auxiliary electrode was used. For cyclic voltammetry, the cell with mercury pool auxiliary electrode and with the distance between DME and the end of the frit-tube minimalized to about 1 mm was used.

Visible spectra were measured on Unicam SP 800B spectrometer.

Experimental Method

Oxygen and moisture free THF was distilled from the sodium metal–benzophenone mixture under argon atmosphere directly into a closed burette. THF may then be transferred from the burette to the vacuable electrochemical cell or to a Schlenk-type apparatus under argon atmosphere without any contact with air. The reactants were either dissolved directly inside the cell or in the closed burette from which their solutions were added to the apparatus under argon atmosphere. Spectral cell was closed by a Rotaflo valve and connected with the apparatus by a removable glass tube. This connection allows to fill the cell in argon atmosphere, to close it and transfer into the spectrometer.

Results

General Approach

Trianions Mmnt$_2^{3-}$ (M = Rh, Co, Ni) are extremely strong reducing agents, very difficult to handle. However, as they are readily formed as primary products of electrochemical reduction of corresponding dianions [5–7] there is an obvious possibility of studying their chemical reactions as processes following the primary electrode reaction [9].

Any chemical reaction of the primary product can be followed electrochemically by measuring the amount of the primary product formed and, in suitable cases, by following the electrochemical behaviour of the species formed in the follow-up chemical reactions. As we were looking for a product of metal-protonation it was reasonable to expect the formation of a new polarographic wave at negative potentials. Complexes with M–H bond are namely known [9–11] to produce reduction waves shifted to more negative potentials with respect to the waves of parent, unprotonized, complexes.

Pivalic acid and phenol were used as sources of protons. Both these compounds are electrochemically inactive in THF solutions. They do not react with starting compounds, *i.e.* Rhmnt$_2^{2-}$, Comnt^{2-} and Nimnt$_2^{2-}$, as was proved spectroscopically.

Polarography of Rhmnt$_2^{2-}$ in the Presence of Weak Acids

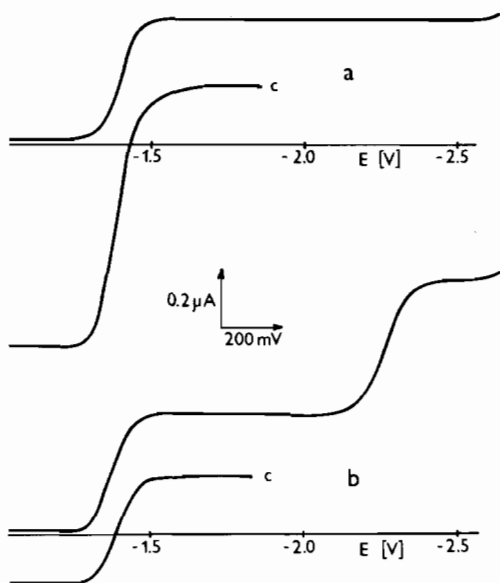Rhmnt$_2^{2-}$ is reduced in a single one-electron fully reversible wave at $E_{1/2}$ = –1.37 V *vs.* SCE [6] (Fig.

Fig. 1. Influence of pivalic acid on polarographic reduction of $Rhmnt_2^{2-}$. a) 7.2×10^{-4} mol l^{-1} [Bu_4N]$_2$[$Rhmnt_2$], 0.1 mol l^{-1} Bu_4NPF_6, THF; b) in presence of 5.6×10^{-4} mol l^{-1} of pivalic acid; c) commutated waves after correction for capacity current, generation potential -1.65 V.
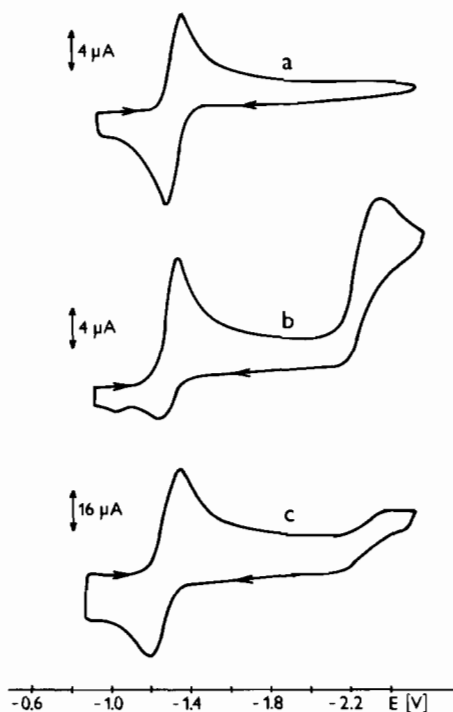

Fig. 2. Cyclic voltammetry of $Rhmnt_2^{2-}$ in presence of pivalic acid. a) 8×10^{-4} mol l^{-1} [Bu_4N]$_2$[$Rhmnt_2$], 0.1 mol Bu_4NPF_6, THF, 10 Vs^{-1}; b) in presence of 9.5×10^{-4} mol l^{-1} of pivalic acid, 20 Vs^{-1}; c) solution b, 200 Vs^{-1}.

1). Primary product of this reduction, *i.e.* $Rhmnt_2^{3-}$, is fairly stable in the THF solution [6].

The influence of the addition of pivalic acid on the polarographic behaviour of $Rhmnt_2^{2-}$ is shown in Fig. 1. The corresponding cyclic voltammogram is shown in Fig. 2.

Characteristic features of the electrochemical behaviour of $Rhmnt_2^{2-}$ in the presence of weak acid may be summarized as follows:

a) Cyclic voltammetry anodic peak belonging to the redox process at -1.37 V strongly decreases upon addition of pivalic acid (Fig. 2). The ratio of commutated to diffusion current, $\bar{i}_c/\bar{i}_d$ (Fig. 1, curve c), decreases substantially from its original value. These results prove a fast follow-up chemical reaction of the primary product, $Rhmnt_2^{3-}$, with the acid.

b) Limiting current of the wave corresponding to the reduction of $Rhmnt_2^{2-}$ does not change upon addition of the acid, *i.e.* the follow-up reaction is not a simple reoxidation process regenerating $Rhmnt_2^{2-}$.

c) New wave at -2.28 V *vs.* SCE arises upon addition of the pivalic acid (Fig. 1). Limiting current of this wave is proportional to the concentration of the acid (Fig. 3)*.
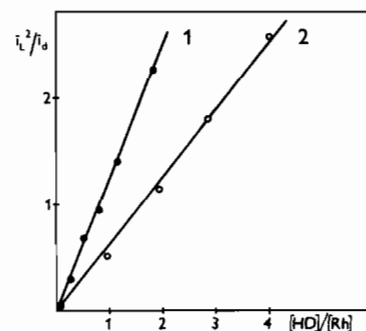

Fig. 3. Dependence of the ratio of limiting currents of $Rhmnt_2^{2-}$ waves on the concentration of the acid. Conditions as in Fig. 1. Curve 1: pivalic acid; curve 2: phenol.

Identical results are observed when phenol is added instead of pivalic acid. As both acids are polarographically inactive and as the components of the solution do not interact, the wave at -2.28 V must belong to the *reduction of a product of a chemical reaction between $Rhmnt_2^{3-}$* (formed at the electrode surface) *and the acid*. Following the arguments, mentioned above, it may be assumed that this chemical reaction is a protonation of $Rhmnt_2^{3-}$.

d) The slope of the dependence of the limiting current upon the concentration of the acid (Fig. 3) is greater in the case of pivalic acid than in the case of phenol, *i.e.* greater concentrations of phenol must be used to achieve the same effect. The limiting current

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*In Fig. 3, the limiting current of the wave at -2.28 V, $\bar{i}_2^2$, is normalized to the value of the limiting diffusion current of the 1st wave, $\bar{i}_d$, which is constant.

is diffusion-controlled in the case of pivalic acid but it has semikinetic character when phenol is used. This shows that the rate of protonation of $Rhmnt_2^{3-}$ depends on the strength of the acid being smaller for weaker acid.

e) For the reduction process at -2.28 V only cathodic peak was observed on cyclic voltammograms (Fig. 2). The ratio of peak currents i_p^2/i_p^1 (i_p^1 corresponds to the more positive diffusion controlled process) decreases with increasing sweep rate (Figs. 2 and 4). This decrease proves that the wave at -2.28 V is due to the reduction of the product of the follow-up reaction of the original electrode reaction at -1.37 V.
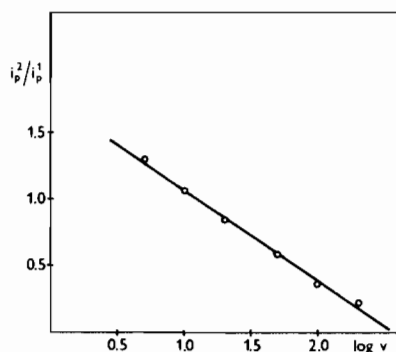

Fig. 4. Dependence of the ratio of voltammetric peak currents of $Rhmnt_2^{2-}$ on sweep rate. i_p^1, peak current of the first reduction step; i_p^2, peak current of the second reduction step; v, sweep rate (Vs^{-1}). Conditions as in Fig. 2, curve b.

f) The reduction wave at -2.28 V corresponds to the electrochemically and chemically irreversible process as follows from the log $\bar{i}/(\bar{i}_d - \bar{i})$ *vs.* E plot (linear, slope 77 mV) and from the complete absence of the corresponding cyclic voltammetry anodic peak (Fig. 2).
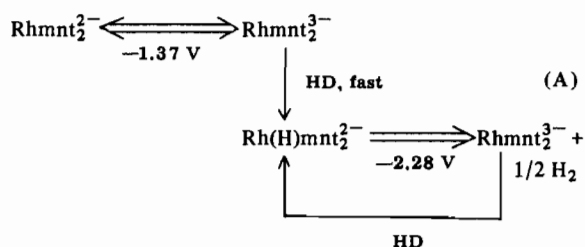
g) The limiting current of the wave at -2.28 V increases with increasing acid concentration above the value of limiting current of the first reduction wave. This means that, at greater acid concentration, the product of the electrode process at -2.28 V reacts also with the acid to regenerate the protonated species. This points to the conclusion that the product of this electrode process is again $Rhmnt_2^{3-}$, *i.e.* process at -2.28 V may be looked at as a hydrogen evolution from the protonated species. This was proved by the Kalousek commutator experiment performed with the solution containing pivalic acid in the concentration 1.24 times greater than the concentration of $Rhmnt_2^{2-}$: The wave at -1.37 V corresponding to the reversible reduction of $Rhmnt_2^{2-}$ to $Rhmnt_2^{3-}$ was commutated at first from generation potential $E_g = -1.55$ V and then from generation potential $E_g = -2.50$ V. In the first case, when only reduction of $Rhmnt_2^{2-}$ to $Rhmnt_2^{3-}$ takes place at the genera-

tion potential, the value of $\bar{i}_c/\bar{i}_d$ was 0.68 corresponding to almost complete consumption of $Rhmnt_2^{3-}$ by its chemical reaction with pivalic acid. However, when $E_g = -2.50$ V is used, the value of $\bar{i}_c/\bar{i}_d$ ratio measured again for the wave at -1.37 V increases to about 1.0. At generation potential -2.5 V, the protonated species is also reduced at the electrode and the increase of $\bar{i}_c/\bar{i}_d$ means that the concentration of $Rhmnt_2^{3-}$ at the electrode surface is, under these conditions, greater than in the case when only $Rhmnt_2^{2-}$ is reduced during the generation period. This implies that $Rhmnt_2^{3-}$ is formed both by the reduction of $Rhmnt_2^{2-}$ and by the reduction of the protonated species.

Similar irreversible hydrogen evolution was observed in the case of several other transition metal hydrides (examples in [9, 10]) and in the case of metal carbonylhydrides [20].

Based on these analogies, we may conclude, that the *protonated species is a compound containing Rh–H bond, i.e. a hydride* $[Rh(H)mnt_2]^{2-}$. Protonation at some other atom than Rh in the $Rhmnt_2^{3-}$ complex is very improbable as hydrogen evolution from such a compound would occur more negatively than that from pivalic acid alone, *i.e.* beyond observable potential range. Furthermore, such a protonated compound would be rather unstable toward dissociation of protonated ligand and no simple reduction leading to $Rhmnt_2^{3-}$ would be observed.

Summarizing these observations, the overall mechanism of the reduction of $Rhmnt_2^{2-}$ in the presence of weak acid (HD) may be explained as follows: $Rhmnt_2^{2-}$ is reversibly reduced at -1.37 V to $Rhmnt_2^{3-}$. This trianion reacts with the acid forming the hydride, $[Rh(H)mnt_2]^{2-}$. This hydride is irreversibly reduced at -2.28 V to hydrogen and $Rhmnt_2^{3-}$, which reacts with the excess of the acid to regenerate the hydride (see Scheme A):

$$Rhmnt_2^{2-} \xrightleftharpoons[-1.37\ V]{} Rhmnt_2^{3-}$$

$$\downarrow \text{HD, fast} \qquad (A)$$

$$Rh(H)mnt_2^{2-} \xrightarrow{-2.28\ V} Rhmnt_2^{3-} + \tfrac{1}{2}H_2$$

$$HD$$

The experimental data do not exclude the possibility that the protonation reaction in scheme (A) is essentially an equilibrium shifted to the protonated species.

Polarography of Comnt$_2^{2-}$ in the Presence of Weak Acids

$Comnt_2^{2-}$ is reduced in a single one-electron reversible wave at -1.83 V *vs.* SCE. Product of this reduction, $Comnt_2^{3-}$, is stable [5].

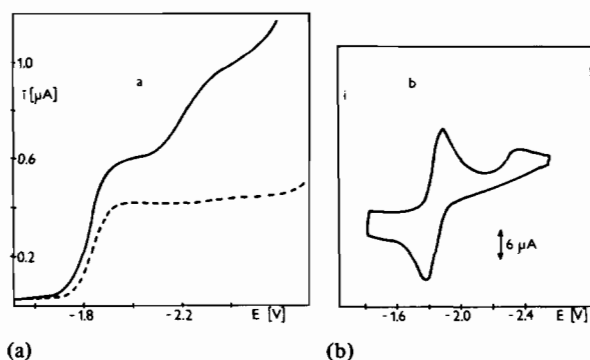(a)   (b)

Fig. 5. Influence of pivalic acid on reduction of $Comnt_2^{2-}$. a) Polarographic curves : dashed curve, 7.5×10^{-4} mol l^{-1} $[Bu_4N]_2[Comnt_2]$, 0.1 mol l^{-1} Bu_4NPF_6, THF; full curve, in presence of 1.51×10^{-3} mol l^{-1} pivalic acid. b) Cyclic voltammogram: 9×10^{-4} mol l^{-1} $[Bu_4N]_2[Comnt_2]$, 0.1 mol l^{-1} Bu_4NPF_6, 3.2×10^{-3} mol l^{-1} pivalic acid, THF, sweep rate 20 Vs^{-1}.
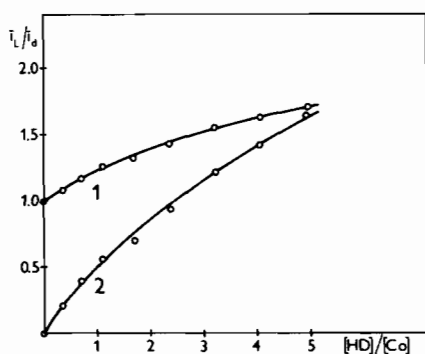

Fig. 6. Dependence of the limiting (i_L) current of the first wave (curve 1) and of the second wave (curve 2) of reduction of $Comnt_2^{2-}$ on the concentration of pivalic acid. Conditions as in Fig. 5a. i_d = limiting current of $Comnt_2^{2-}$ in absence of pivalic acid.

Addition of pivalic acid has the same effect on the polarographic and voltammetric behaviour of $Comnt_2^{2-}$ as in the case of the rhodium complex. New irreversible wave at $E_{1/2} = -2.21$ V vs. SCE is formed upon addition of pivalic acid (Fig. 5). It may be concluded, as in the case of rhodium complex, that $[Co(H)mnt_2]^{2-}$ is formed by the protonation of $Comnt_2^{3-}$. This cobalt protonated species is also reduced to $Comnt_2^{3-}$ and hydrogen.

However, there are two important differencies between the behaviour of cobalt and rhodium compounds:

a) As follows from comparison of Fig. 3 and Fig. 6, the limiting current of the more negative wave of the cobalt complex increases with acid concentration more slowly than in the case of rhodium complex and it becomes reaction rate controlled in the excess of the acid. The decrease of the $\bar{i}_c/\bar{i}_d$ ratio (measured at

the more positive wave) due to the addition of the acid is less than in the case of rhodium (Rh = 0.68, Co = 1.4 at acid concentration 1.24 times greater than complex concentration). These results point to the conclusion that the protonation reaction of the cobalt complex is slower than in the case of rhodium and the equilibrium seems to be shifted less to the protonated species*.

b) Limiting current of the wave corresponding to the primary reduction of $Comnt_2^{2-}$ increases also with increasing acid concentration and becomes partially reaction rate controlled (Figs. 5, 6; curve 1). This indicates that $[Co(H)mnt_2]^{2-}$ formed in the follow-up reaction decomposes spontaneously to $Comnt_2^{2-}$ and 1/2 H_2. Regeneration of $Comnt_2^{2-}$ is thus the reason for the increase of the limiting current of the more positive wave.

Scheme B is consistent with the experimental data:
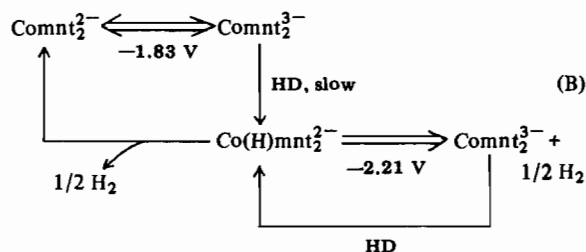
However, mechanism assuming slow outer-sphere oxidation of $Comnt_2^{3-}$ species by weak acid parallel to the formation of the $[Co(H)mnt_2]^{2-}$ instead of the decomposition of the latter species would also be consistent with experimental data. The decomposition reaction shown in scheme (B) seems, however, more probable by analogy with the rhodium protonated complex for which such a process was observed in solution.

Polarography of $Nimnt_2^{2-}$ in the Presence of Weak Acids

$Nimnt_2^{2-}$ is reduced in single one-electron reversible wave at $E_{1/2} = -1.87$ V vs. SCE. Product of this reduction, $Nimnt_2^{3-}$, is stable [3].

Figure 7 shows the influence of the acid on the polarographic behaviour of $Nimnt_2^{2-}$. The only observed effect is the increase of the limiting current of the reduction wave at -1.87 V. The dependence of the limiting current of the acid concentration is shown in Fig. 8. The increase of the limiting current is rather small even at relatively high acid concentrations. No new wave arises upon acid addition. There are two possible mechanisms consistent with the experimental data:

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*Unless equilibrium constants are known independently it is not possible to distinguish unambiguously rate and equilibrium effects solely from polarographic measurements.
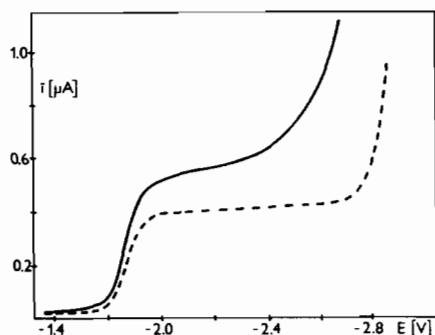
Fig. 7. Influence of pivalic acid on reduction of $Nimnt_2^{2-}$: dashed curve, 6.8×10^{-4} mol l^{-1} $[Bu_4N]_2[Nimnt_2]$, 0.1 mol l^{-1} Bu_4NPF_6, THF; full curve, in presence of 3×10^{-3} mol l^{-1} pivalic acid.
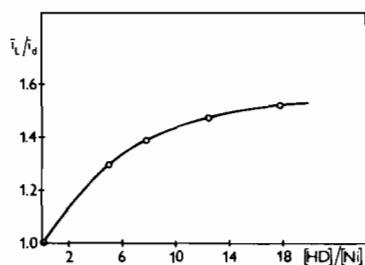

Fig. 8. Dependence of the limiting current (i_L) of $Nimnt_2^{2-}$ on concentration of pivalic acid. Conditions as in Fig. 7. i_d = limiting current of $Nimnt_2^{2-}$ in the absence of pivalic acid.

a) $Nimnt_2^{3-}$ is slowly oxidized by the acid directly to $Nimnt_2^{2-}$

b) $Nimnt_2^{3-}$ reacts slowly with the acid forming $[Ni(H)mnt_2]^{2-}$ which very rapidly decomposes to $Nimnt_2^{2-}$ and H_2.

Experimental data cannot distinguish between these two possibilities.

$[Rh(H)mnt_2]^{2-}$ in the Solution

It is possible to prepare THF solutions of $[Rh(H)mnt_2]^{2-}$, which are fairly stable in rigorous absence of oxygen: The deep green solution of $(Bu_4N)_2[Rhmnt_2]$ in THF is titrated by the THF solution of $LiAlH_4$ till the stable wine red colour of $Rhmnt_2^{3-}$ appears [6]. Small volume of concentrated THF solution of pivalic acid is then rapidly added in one portion. The total amount of added pivalic acid has to be 50–80 times greater than the amount of the rhodium complex to decompose all unreacted $LiAlH_4$. After addition of pivalic acid, the colour of the solution turns red-brown. The resulting solution shows a single reduction wave at -2.28 V proving thus the identity of the chemically prepared species with electrochemically observed intermediate $[Rh(H)mnt_2]^{2-}$. The polarographic experiment was performed in the presence of the excess of Bu_4NCl.

The Li^+ ions arising from $LiAlH_4$ form thus LiCl sparingly soluble in THF and the eventual reduction wave of Li^+-ions is very small and does not interfere.

The solutions of $[Rh(H)mnt_2]^{2-}$ are extremely air-sensitive. They react immediately with traces of air to give green solutions of $Rhmnt_2^{2-}$, characterized spectroscopically by the absorption band at 640 nm (Fig. 9).
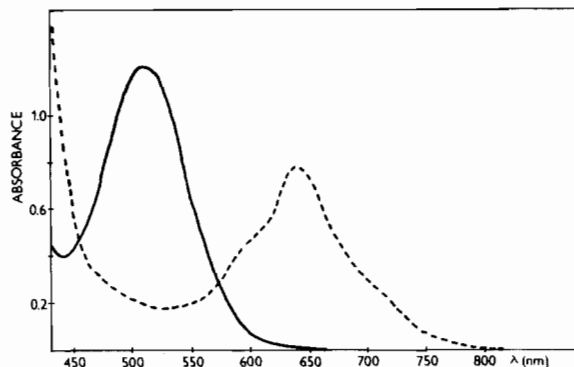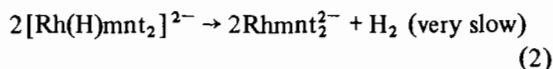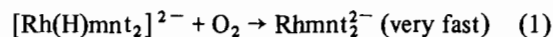

Fig. 9. Absorption spectrum of $Rhmnt_2^{2-}$ (dashed line) and $Rhmnt_2^{3-}$ (solid line). Concentration: 2.13×10^{-4} mol l^{-1}.

$[Rh(H)mnt_2]^{2-}$ prepared by the above procedure may be characterized by absorption band at 464 nm, $\epsilon = 3700$ (Fig. 10, curve 1). As follows from Fig. 10, $[Rh(H)mnt_2]^{2-}$ decomposes very slowly even in absence of oxygen producing $Rhmnt_2^{2-}$ (cf. Fig. 9 for comparison with the spectra of $Rhmnt_2^{2-}$ and $Rhmnt_2^{3-}$).

Hence, following reactions are characteristic for $[Rh(H)mnt_2]^{2-}$:

$$[Rh(H)mnt_2]^{2-} + O_2 \rightarrow Rhmnt_2^{2-} \text{ (very fast)} \quad (1)$$

$$2[Rh(H)mnt_2]^{2-} \rightarrow 2Rhmnt_2^{2-} + H_2 \text{ (very slow)} \quad (2)$$

From the occurrence of reactions (1) and (2) it follows that protonation of $Rhmnt_2^{3-}$ is not connected with great structural changes in $Rhmnt_2$ unit. No evidence for mnt ligand dissociation was found. Thus, solution properties of $[Rh(H)mnt_2]^{2-}$ are in full agreement with the above formulation of this compound as complex with Rh–H bond.

Reaction of $Rhmnt_2^{2-}$ and $Comnt_2^{2-}$ with Stronger Acids

Benzoic and stronger acids oxidize $Rhmnt_2^{2-}$ and $Comnt_2^{2-}$ to $[Rhmnt_2]_n^{n-}$ and $[Comnt_2]_2^{2-}$, respectively. Absorption spectra of these species obtained by oxidation with the acids are identical with the spectra of species obtained by iodine or oxygen oxidation [25]. Benzoic acid oxidizes $Rhmnt_2^{3-}$ directly to $[Rhmnt_2]_n^{n-}$.
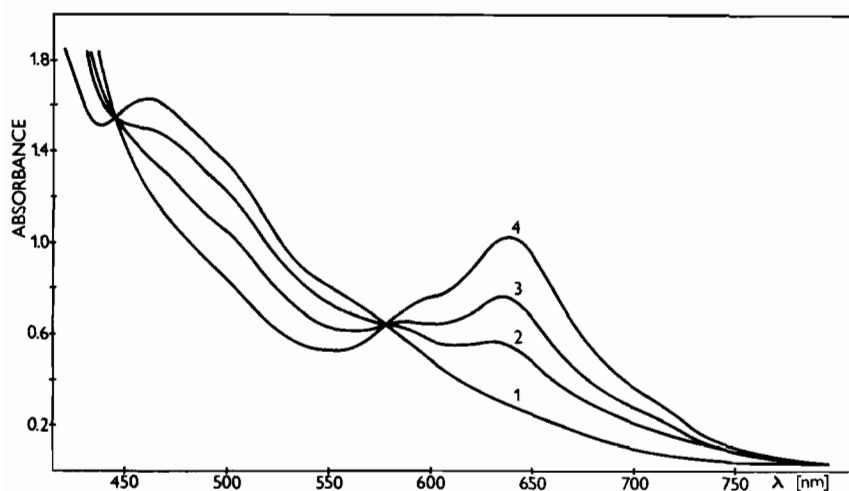
Fig. 10. Time-dependence of absorption spectrum $Rh(H)mnt_2^{2-}$. Concentration, 4.8×10^{-4} mol l^{-1}: curve 1, t = 0; 2, t = 75 min; 3, t = 165 min; 4, t = 360 min.

Reaction of $Mmnt_2^{3-}$ *(M = Rh, Co, Ni) with* C_6H_5Cl, C_6H_5Br

Addition of great excess of phenyl halides to the solution of $Mmnt_2^{2-}$ complexes does not lead to any reaction in the solution nor to any change in the electrochemical behaviour of these compounds. The primary products of the electrode reaction, *i.e.* $Mmnt_2^{3-}$ complexes, do not react even in the presence of great excess of phenyl-halides under conditions of the polarographic experiment.

Discussion

The electrochemical evidence quoted above points to the conclusion that $Mmnt_2^{3-}$ (M = Rh, Co) complexes react with weak protonic acids under the formation of metal-protonated species, $[M(H)mnt_2]^{2-}$. The $Mmnt_2$-unit is preserved in the protonated species without any substantial changes and can be looked upon as a Lewis base. This follows from the observed hydrogen evolution at dropping mercury electrode which is identical with that characteristic *e.g.* for metal—carbonyl hydrides (20, 28). $Rhmnt_2^{3-}$ is a stronger base, reacting faster and having the equilibrium shifted more to the side of the protonized species than the analogous cobalt complex. However, the type of metal—hydrogen interaction is essentially the same in both cases. The formation of a protonated Ni complex has not been proved. If a Ni protonated complex is formed at all its inherent stability is so low that it immediately disproportionates into hydrogen and $Nimnt_2^{2-}$, *i.e.* phenomenologically an oxidation results.

$[Rh(H)mnt_2]^{2-}$

Important feature of $[Rh(H)mnt_2]^{2-}$ complex, bringing an insight on the nature of metal—hydrogen bond, is its redox behaviour: This compound is, on one side, reduced electrochemically to $Rhmnt_2^{3-}$, *i.e.* to a species containing formally univalent rhodium, and, on the other side, it can be oxidized by oxygen to $Rhmnt_2^{2-}$, *i.e.* to a compound of formally divalent rhodium*. Thus both reduction and oxidation result in the rupture of Rh—H bond. The redox active center involved is obviously the Rh—H unit which can be regarded as being in the 'dynamic redox state' [10].

The rhodium—hydrogen interaction proceeds via the metal d_{z^2} orbital, the highest occupied MO in the $Rhmnt_2^{3-}$ unit fully available for axial bonding of simple σ-Lewis acids. This interaction is of the *acid—base* type without any complete electron transfer between metal and hydrogen: The hydrogen-ligand retains, obviously, partially its protonic character, as follows from the ability of the complex to undergo electrochemical hydrogen evolution.

The metal-d_{z^2} orbital is only weakly involved in the bonding of the metal with mnt-ligands and its involvement in an axial bond (Rh—H) would not destabilize the $Rhmnt_2$-unit, as it is not involved in the out-of-plane π-bonding. On the other hand, the partial decrease of negative charge on the metal due to the binding of a proton would tend to stabilize most of the metal-based molecular orbitals.

The corresponding oxidation and reduction process involve only the bonding and antibonding orbitals of the Rh—H bond, respectively. They are highly localized (rhodium d_{z^2} and hydrogen 1s orbitals) and, due to weak involvement of the d_{z^2} orbital in the bonding within the $Rhmnt_2$-unit any electron change in these orbitals cannot be compen-

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*As this oxidation proceeds very rapidly even in large excess of free proton donor the reaction path via $Rhmnt_2^{3-}$ in equilibrium with $[Rh(H)mnt_2]^{2-}$ seems to be very unlikely.

sated for by electron drift from or to the mnt-ligands and rupture of the metal—hydrogen bond in both oxidation and reduction thus results. In $Comnt_2^{3-}$ the d_{z^2}, predominantly metal localized, orbital is not the highest occupied orbital [22, 27]. In spite of this, d_{z^2}-orbital is still the most suitable basic site of the complex, its interaction with proton is, however, less favourable than in the case of the rhodium complex. This is fully supported by the experimental facts described above.

Ability of Planar Dithiolene Complexes for Substrate Addition

The described behaviour of $Mmnt_2^{3-}$ (M = Rh, Co) complexes is in full agreement with the prediction based on the theoretical analysis using simple pertur-bation method [1]. Except for NO [2], no other redox addition or Lewis acid coordination was described previously for any of $Mmnt_2^{n-}$ complexes. In this respect the behaviour of planar dithiolene complexes contrasts with that of other planar com-plexes of Rh(I) or Co(I). *E.g.* the Vaska type com-plexes are known to react with a wide variety of sub-strates via redox-addition mechanism. With protonic acids, six-coordinate Rh(III)—hydride complexes are readily formed. Even $[Rh(CO)(PEt_3)(mnt)]^-$ reacts with perchloric acid in the presence of free PEt_3 under the formation of $[Rh(H)(CO)(PEt_3)_2(mnt)]$ as has been described recently [23]. The observed difference is obviously connected with the presence of two mnt ligands in the coordination sphere.

The Co(I)—Schiff-base planar complexes are also known to undergo redox addition reactions, *e.g.* with C_6H_5Cl or C_6H_5Br forming Co(III)—organometallic species [21]. Analogous reaction of $Comnt_2^{3-}$ does not proceed in spite of the fact that the latter complex is a much stronger reducing agent than the analogous Shiff-base complexes [21].

The essential factor for a redox addition process of square planar complexes seems to be the availabili-ty of the p_z-orbital for effective axial bonding [29] and achievement of coordination number six. In all planar bis-dithiolene complexes the p_z orbital is, how-ever, strongly involved in the out-of-plane π-bonding [8, 26, 27], the most important being its interaction with occupied b_{1u} ligand π-group orbital which has a strong stabilizing effect. The p_z orbital is essential in mediating the ligand—ligand interaction and deloca-lization of the π-system over the whole molecule. This strong ligand—ligand interaction is the main factor governing the ability of mnt-complexes to form extensive redox series [30]. On the other hand, the involvement of the p_z orbital in the delocalized π-system makes it unavailable for mixing with d_{z^2} orbital and thus for the formation of effective axial bonds. The loss of stabilization energy which would arise from the decrease of ligand—ligand interaction via the p_z orbital, in case this orbital would get

involved in axial bonding, could be hardly compen-sated for by the newly formed axial bonds. The expected interaction of low-valent square planar bis-dithiolene complexes is thus limited to simple outer-sphere electron-exchange processes, mainly localized in the π-system, or to a Lewis acid—base interaction with the d_{z^2}-orbital under the formation of a species with coordination number five. The oxidative addi-tion of NO [2] is a special case as this ligand is able to interact with the π-system of the $Mmnt_2$-unit without its substantial destabilization.

The experimental data as well as theoretical calcu-lations [5, 7, 27] show that the reduction of $Mmnt_2^{3-}$ to corresponding trianions is connected with considerable destabilization of all molecular orbitals with greater participation of metal orbitals and, at the same time, with an increase of metal character of these orbitals, the high-lying d-based MO's being destabilized to a greatest extent [5, 7, 27]. The addi-tion of a σ-Lewis acid to the metal center opposes this destabilizing influence mainly due to the decrease of the excess electron density on the central atom and by stabilizing the occupied d_{z^2} based MO. This stabilization of the $Mmnt_2^{3-}$ unit by formation of an adduct with σ-Lewis-acids increases with increasing orbital energy of d_{z^2}-based MO in $Mmnt_2^{3-}$ com-plexes. The basicity of $Mmnt_2^{3-}$ complexes increases with their increasing ability to be stabilized by σ-Lewis acid coordination. The order of increasing basicity of $Mmnt_2^{3-}$ complexes is thus identical with the order of increasing energy of the d_{z^2}-based MO. The basicity of $Mmnt_2^{3-}$ complexes thus decreases in the order Rh > Co > Ni, which is also, as mentioned above, the order of the energy of the d_{z^2} orbitals in the corresponding complexes [22, 27]. In the nickel complex, the HOMO is the d_{xy}-based molecular orbital [4] and the, predominantly metal localized, d_{z^2} orbital is energetically very stable and only slightly affected by the formation of the trianion [27]. This makes the metal center in the nickel com-plex rather weakly basic and, at the same time, susceptible to electron exchange processes, in full accordance with experimental findings.

The basicity of the central metal atom in $Comnt_2^{3-}$ complex is greater than that of analogous Ni-species as the d_{z^2} orbital in the former case is more affected by the reduction of the dianion to trianion. However, the d_{z^2} is not a HOMO of the complex as it is in the case of the Rh-complex. Therefore, the basicity of the $Comnt_2^{3-}$ is lower than that of the $Rhmnt_2^{3-}$ complex.

Conclusion

In accordance with theoretical prediction, $Mmnt_2^{3-}$ (M = Rh, Co, Ni) complexes were found to be rather unreactive in redox addition reactions in spite of

being very strong reducing agents. Metal centers in Rh and Co moieties show, however, a considerable Lewis-basicity which leads to coordination of acidic hydrogen atom to the metal under the formation of hydride-type complexes $[M(H)mnt_2]^{2-}$ (M = Rh, Co) in which the hydrogen preserves partially protonic character. This interaction introduces a new, rather localized, redox-active center into the molecule. The best formulation of these hydride-like complexes seems to regard them as protonized species of univalent metals. The described behaviour indicates a general picture explaining the essential features of the reactivity of low-valent square-planar bis dithiolene complexes which is strongly influenced by the involvement of the metal p_z-orbital in the π-system of the whole complex unit.

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