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Reaction of Transition Metal Bis(malconitriledithiolato) Complexes, $\mathrm{Mmmt}_2^{2-,\cdot-}$ (M = Co, Ni, Cu, Rh) with Methyl Iodide

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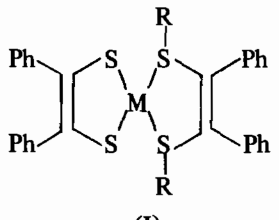
Mmnt_2^{2-} (M = Co, Ni, Cu, Zn) complexes react with CH_3I, both mnt ligands being methylated on all sulphur donor atoms. The methylation products decompose and free Me_2mnt is formed. Kinetics of this reaction were followed. The rate determining step is methylation of first sulphur aom in the complex, the rate constants being of the order 10^{-3} $l\ mol^{-1}\ s^{-1}$. Corresponding monoanions, Mmnt_2^{-} (M = Co, Ni, Cu) decompose only extremely slowly in the presence of CH_3I. Rhmnt_2^{2-} complex is rapidly oxidized by CH_3I with no methylation of sulphur donor atoms.

Introduction

Reactions of four-coordinated square-planar transition metal complexes of 1,2-dithiolato* ligands with alkyl halides attracted much interest [1–9] since G. N. Schrauzer [1] described the alkylation of $[M(S_2C_2Ph_2)]^{2-}$ (M = Ni, Pd, Pt) which results in thioether species of the type $[M(R_2S_2C_2Ph_2)(S_2C_2Ph_2)]$ (I).



(I)

Six-coordinated complexes $[M(S_2C_2Ph_2)_3]^{2-,\cdot-}$ (V, Mo, W, Re) react with alkyl halides in the same way [1–3].

These alkylation reactions are regarded as a probe of the nucleophilicity of the sulphur donor atoms [1–9]. It is generally accepted that sulphur atoms are sufficiently strong nucleophiles only in such complexes which may be regarded as having coordinated dianionic 1,2-dithiolato ligands $S_2C_2R_2^{2-}$ (R is an electron-donating substituent, *i.e.* Ph, alkyl). In this sense, the methylation of bis- as well as tris-(1,2-dithiolato) complexes by methyl iodide is used as an indication of the dianionic nature of the dithiolene ligand. Occupation of ligand-based MOs in dithiolene complexes may be thus deduced from the occurrence of the methylation reaction localized on sulphur atom [2]. However, Schrauzer found the complex of maleonitriledithiolato ligand, Nimnt_2^{2-}, which is isoelectronic with $[Ni(S_2C_2Ph_2)_2]^{2-}$, to be unreactive towards CH_3I [1]. It was stated [2], that sulphur atoms are not sufficiently nucleophilic in complexes of dianionic ligands, $S_2C_2R_2^{2-}$, where R is an electron-withdrawing substituent, *e.g.* –CN, $-CF_3$. These substituents have been believed to decrease the electron density on sulphur donor atoms making them unreactive towards alkyl halides.

However, recently it was found that mnt^{2-} dianion can be methylated when it is coordinated to Pb(II) [5] or, more slowly, in the form of the disodium salt, Na_2mnt [5, 6]. Eisenberg described methylation of one sulphur donor atom in Rh(I) complexes, $[Rh(diene)mnt]^-$ and $[Rh(CO)(PPh_3)mnt]^-$, the reaction mechanism being, however, rather complicated [7–9]. These results indicate that the unreactivity of mnt^{2-} and $S_2C_2(CF_3)_2^{2-}$ complexes described by Schrauzer [1, 2] cannot be explained by the inductive effect of the ligand substituent.

Recently, we deduced from the electrochemical data [10–13], in accordance with EPR results [14], that Mmnt_2^{2-} (M = Rh, Co, Ni, Cu, Zn) species may be best described as complexes of formally divalent metals with coordinated *dianionic* mnt^{2-} ligands.

Based on this conclusion on the dianionic nature of mnt-ligand in Mmnt_2^{2-} (M = Rh, Co, Ni, Cu, Zn) complexes, we have predicted that contrary to

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*1,2-dithiolato ligands are $S_2C_2R_2^{2-}$ species. mnt^{2-} = maleonitriledithiolate = cis-1,2-dicyanoethylene-1,2-dithiolate dianion = $S_2C_2(CN)_2^{2-}$. Term 'dithiolene complexes' means complexes of $S_2C_2R_2$ ligands without ligand charge specification.

Schrauzer's findings, these complexes have to undergo the reaction with methyliodide.

To throw light on the problem whether the methylation of sulphur atom is really generally indicative of the dianonic nature of the coordinated dithiolene ligand, we studied reactions of title complexes (whether dianions, $Mmnt_2^{2-}$, or the corresponding monoanions, $Mmnt_2^-$), with methyliodide in THF. To elucidate the nature of this reaction in more detail, kinetics of $Mmnt_2^{2-}$ (M = Co, Ni, Cu) methylation was followed. The results observed were compared with electron density on sulphur atom estimated by iterative EHT method [15]. The comparison of all these results brings new insight on the bonding in square-planar dithiolene complexes.

Experimental

Chemicals

$Na_2mnt = Na_2S_2C_2(CN)_2$ was prepared according to [16], $Rh_2(CH_3COO)_4 \cdot 2CH_3OH$ according to [17].

$[Bu_4N]_2[Rhmnt_2]$ was prepared by modified procedure described in [18]: 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 stiring, 8 ml of the methanolic solution of $[Bu_4N]OH$ (prepared from 5 g Bu_4NCl and methanolic suspension of Ag_2O) was added. A very dark solid precipitated from this mixture at 0 °C, for 20 minutes. This material was filtered-off, washed with isopropyl alcohol, dissolved in 50 ml of acetone, filtered 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 for 1 hr. This solid product was filtered off, washed several times with isopropyl alcohol and finally with pentane and dried *in vacuo*. The product was spectrally and by analysis characterized as $[Bu_4N]_2[Rhmnt_2]$. The yield was 0.46 g, *i.e.* 27% based on $Rh_2(CH_3COO)_4 \cdot 2CH_3OH$. Solid product is air-stable, but its green solutions are readilly oxidized by air to dark brown-red solutions. All described synthetic procedures were performed in a pure argon atmosphere in the Schlenk-type apparatus. All solvents were free of oxygen and were handled in closed apparatus.

$[Bu_4N]_2[Mmnt_2]$; M = Co, Ni, Cu, Zn were prepared according to [19].

$[Bu_4N][Mmnt_2]$ (M = Co, Ni) were prepared by iodine oxidation of $[Bu_4N]_2[Mmnt_2]$ complexes according to [19, 20].

$[Bu_4N][Cumnt_2]$ was prepared by bromine oxidation of $[Bu_4N]_2[Cumnt_2]$. The sample was obtained from Prof. E. Hoyer, Karl-Marx-University, Leipzig, GDR.

CH_3I (Lachema) was purified by distillation freshly before use. Tetrahydrofuran (THF) (Merck): oxygen and moisture free THF was distilled from the sodium metal–benzophenone mixture under argon atmosphere directly into burette closed by a Rotaflo valve.

Instrumentation

Visible and UV spectra were measured on Unicam SP 800B spectrophotometer, which was also used for kinetic measurements. IR spectra were recorded using Perkin-Elmer Model 257 grating spectrophotometer. Samples were examined in the form of KBr pellets. Mass spectra were obtained on Jeol JMS-D 100 Mass spectrometer. Exact values of molecular weights were determined by peak-matching technique with perfluorokerosene as an internal standard. NMR spectra were measured in $CDCl_3$ solutions, with Me_4Si as internal standard, using Jeol FX-60 spectrometer. EPR spectra were obtained with a Varian E-4 X-band spectrometer.

Methylation of $Mmnt_2^{2-}$ Complexes (M = Co, Ni, Cu, Zn)

0.13 g of $[Bu_4N]_2[Mmnt_2]$ was dissolved in 25 ml freshly distilled, oxygen-free THF in Schlenk-type apparatus. To this solution CH_3I (1 ml, ~100-times excess) was added. Over several hours, the colour of the solutions changes: Co, from dark-red to green; Ni, from dark red to wine-red; Cu, from brown-red to orange; Zn, from very light yellow to yellow. After 24 hours of standing at laboratory temperature, the solvent was removed by passing an argon stream through the solution. The resulting paste was dried under reduced pressure. The crude material was extracted in Soxlet apparatus with pentane giving a colourless solution and a coloured microcrystalline solid. IR spectra of the solid products were recorded, proving in all cases that these products do not contain any mnt-ligand or its derivatives (no absorption peak in the range of C≡N-vibration frequencies was observed).

The filtered pentane solution was evaporated to dryness producing yellow powder, which was purified by vacuum sublimation. Resulting yellow crystalline solid was identified as *cis*-1,2-di(methylmercapto)-1,2-dicyanoethylene = $Me_2mnt = (CH_3S)_2C_2(CN)_2$.

This compound was obtained in all cases in 80% yield based on assumption that both mnt-ligands in $Mmnt_2^{2-}$ complexes are methylated. The product before sublimation (~97% yield) is almost pure Me_2mnt; it contains only little traces of free pentane, as proved by mass spectrocopy.

The Me_2mnt product was identified by mass spectral (Fig. 1) molecular weight determination, which gives the molecular weight 169.9977 (calcd.

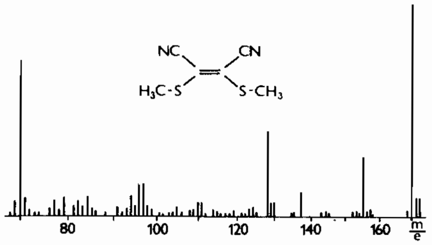

Fig. 1. Mass spectrum of Me_2mnt obtained by $Mmnt_2^{2-}$ methylation.

value 169.9982); the experimental error was 3 ppm. This compound exhibited single ^1H NMR signal occurring at δ = 2.66 ppm (in $CDCl_3$ solution); this value correlates very well with values of chemical shifts of Me_2mnt species and $Memnt^-$-ligand [5–7]. The melting point was identical with that published for Me_2mnt, *i.e.* 99 °C [5, 6].

Reaction of $[Bu_4N]_2[Rhmnt_2]$ *with* CH_3I

0.1 g of $[Bu_4N]_2[Rhmnt_2]$ was dissolved in Schlenk-type apparatus in 40 ml of oxygen-free THF. Pure argon atmosphere was used. 4 ml of CH_3I were added dropwise to the dark green solution of $Rhmnt_2^{2-}$. The colour of the solution changed to dark red-brown immediately after addition of first few drops of CH_3I. The resulting solution was then handled in the same manner as reaction mixtures of other $Mmnt_2^{2-}$ complexes described above, *i.e.* after 24 hours it was evaporated to dryness and resulting dark solid was extracted with pentane. No compound soluble in pentane was present in this solid product. The solid product was heated up to 170 °C in the ion-source of the mass spectrometer. No ions corresponding to Me_2mnt were detected mass-spectroscopically. (Only ions from residual CH_3I and solvents were observed.) Further purification and characterisation of this solid is in progress. Preliminary results show that this product is like the product of oxidation of $Rhmnt_2^{2-}$ by air [22]. ^1H NMR spectra of this compound prove that S–CH_3 bond is not present (no NMR signal for CH_3 was observed at *ca.* 2.60 ppm).

It may be concluded that methylation of $Rhmnt_2^{2-}$ proceeds by different mechanism than methylation of other $Mmnt_2^{2-}$ complexes and that it does not produce Me_2mnt.

Spectral Measurements

Methylation kinetics of $Mmnt_2^{2-}$ (M = Co, Ni, Cu, Zn) complexes, methylation of $Rhmnt_2^{2-}$ and $Mmnt_2^-$ (M = Co, Ni, Cu) complexes were studied by visible and UV absorption spectra. Conventional 1 cm cells were closed by a serum bottle cap. They were filled under argon atmosphere using the syringe technique. Exact amount of CH_3I was added through the serum bottle cap by Hamilton microliter syringe.

Methylation of $Rhmnt_2^{2-}$ was also studied by EPR spectra. The solution of the complex was mixed with CH_3I in a Schlenk-tube under argon atmosphere and then it was transferred into the EPR cell filled with pure argon by syringe technique.

Results

Methylation of $Mmnt_2^{2-}$ *(M = Co, Ni, Cu, Zn) Complexes*

This reaction was examined in THF. It was shown [21] that nucleophilicity of substrates depends on the solvent. THF was chosen as a more suitable solvent than previously used methanol [1, 5] as it can be expected to stabilize the nucleophilic centers by solvation to a much smaller extent than methanol.

As follows from experimental results, all $Mmnt_2^{2-}$ (M = Co, Ni, Cu) complexes react with CH_3I qualitatively in the same way. The products of methylation of all these complexes are identical: crystalline compound, which contain neither mnt ligand nor its derivatives, as was tested by IR. These products are

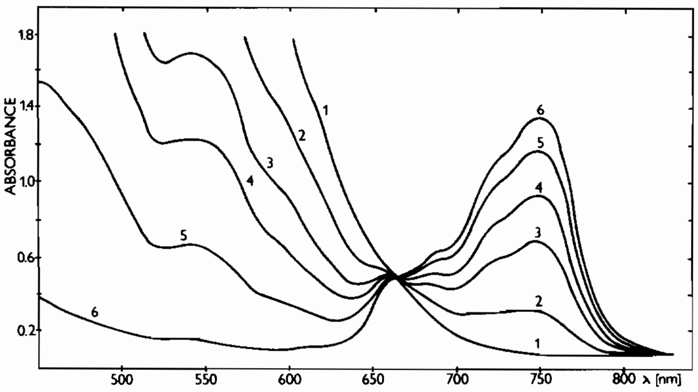

Fig. 2. Methylation kinetics of $Comnt_2^{2-}$. Initial concentrations: $1.31 \cdot 10^{-3}$ mol·l^{-1} $[Bu_4N]_2[Comnt_2]$; $6.18 \cdot 10^{-1}$ mol·l^{-1} CH_3I. Time: curve 1, 0 s; 2, 30 s; 3, 170 s; 4, 300 s; 5, 570 s; 6, completed reaction.

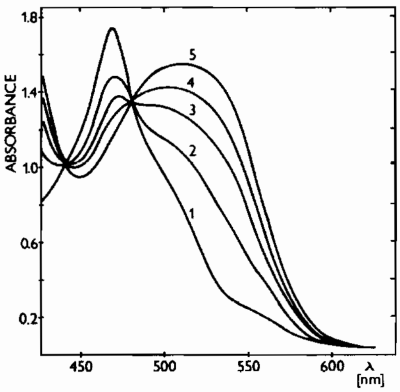

Fig. 3. Methylation kinetics of Nimnt$_2^{2-}$. Initial concentrations: $4.60\cdot10^{-4}$ mol·l^{-1} $[Bu_4N]_2[Nimnt_2]$; $4.84\cdot10^{-1}$ mol·l^{-1} CH_3I. Time: curve 1, 0 s; 2, 260 s; 3, 530 s; 4, 800 s; 5, completed reaction.

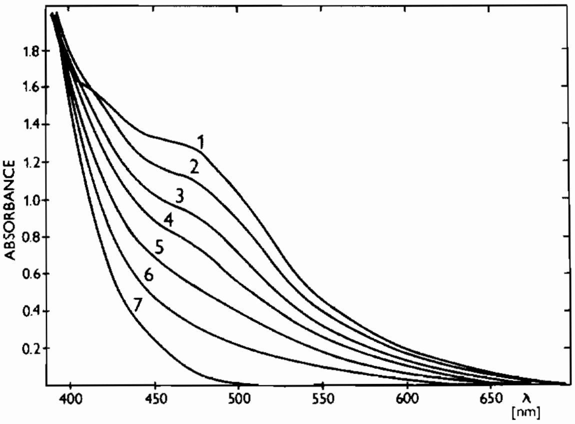

Fig. 4. Methylation kinetics of Cumnt$_2^{2-}$. Initial concentrations: $2.40\cdot10^{-4}$ mol·l^{-1} $[Bu_4N]_2[Cumnt_2]$; $6.43\cdot10^{-1}$ mol·l^{-1} CH_3I. Time: curve 1, 0 s; 2, 28 s; 3, 230 s; 4, 440 s; 5, 740 s; 6, 1250 s; 7, completed reaction.

probably tetraiodo complexes $[Bu_4N]_2[MI_4]$, as was proved by visible absorption spectra in the case of cobalt complexes. The second product was unambiguously characterized as $(CH_3S)_2C_2(CN)_2$ = Me$_2$mnt (Fig. 1), and is formed in nearly stoichiometric yield (reaction 1):

$$\mathrm{Mmnt}_2^{2-} + 4\mathrm{CH_3I} \rightarrow 2\mathrm{Me_2mnt} + \mathrm{MI}_4^{2-} \qquad (1)$$

The yields of Me$_2$mnt as well as IR-spectral characterization of the solid product prove that *both mnt^{2-} ligands in Mmnt$_2^{2-}$ complexes react with CH_3I and all four sulphur atoms are methylated.* Non-transition metal complex, Znmnt$_2^{2-}$, reacts with CH_3I in the same manner producing free Me$_2$mnt as the main reaction product.

TABLE I. Rate Constants of Mmnt$_2^{n-}$ Methylation and Changes on Sulphur Atoms.

Compound	k[a]	q[b]
Comnt$_2^{2-}$	$9.21\cdot10^{-3}$	−0.256
Comnt$_2^{-}$	c	−0.078
Nimnt$_2^{2-}$	$6.45\cdot10^{-3}$	−0.267
Nimnt$_2^{-}$	c	−0.088
Cumnt$_2^{2-}$	$2.32\cdot10^{-3}$	−0.131
Cumnt$_2^{-}$	c	−0.097

[a] Rate constants in l mol^{-1} s^{-1}. [b] Charges on sulphur atoms estimated by iterative EHT [15]. [c] Methylation reaction, if proceeds, is extremely slow.

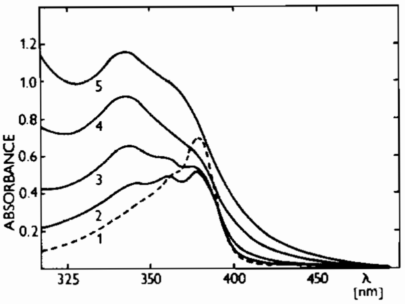

Fig. 5. Methylation kinetics of Znmnt$_2^{2-}$. Initial concentrations: $2.98\cdot10^{-5}$ mol·l^{-1} $[Bu_4N]_2[Znmnt_2]$ $3.15\cdot10^{-1}$ mol·l^{-1} CH_3I. Time: curve 1, 0 s; 2, 180 s; 3, 420 s; 4, 780 s; 5, completed reaction.

Kinetics of Mmnt$_2^{2-}$ Methylation

Kinetics of reaction between Mmnt$_2^{2-}$ (M = Co, Ni, Cu, Zn) and CH_3I in THF was studied spectrophotometrically in visible or UV region. Typical spectral records of these kinetic rules are shown in Figs. 2–5. Time changes of absorbance were measured at following wavelengths: Co: 750 nm; Ni: 530 nm; Cu: 470 nm. Absorbance at time t, A, is related to the extent of the reaction, x, through the relationship

$$x/a = (A - A_o)/(A_\infty - A_o),$$

where a is the initial concentration of Mmnt$_2^{2-}$ complex, A_o and A_∞ are initial and final absorbance at given wavelength, respectively. The 1st order of the reaction with respect to Mmnt$_2^{2-}$ was proved in the case of Co, Ni and Cu complexes by linear correlation of ln a/(a − x) *vs.* time (Fig. 6) obtained under the conditions of pseudo-1st-order reaction, *i.e.* when great molar excess of CH_3I was used. This correlation is perfectly linear for M = Co, Ni and Cu complexes in all the range of CH_3I-concentrations used. The slope of the ln a/(a − x)–t plot is equal to the apparent pseudo-1st-order rate constant, k′. To evaluate the reaction order with respect to methyliodide, dependence of k′ on CH_3I concentration was measured. It was shown (Fig. 7) that for Co, Ni and Cu complexes the plot of k′ *vs.* CH_3I is linear, prov-

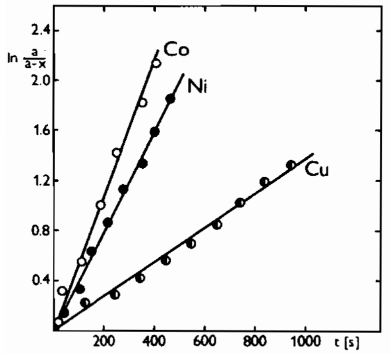

Fig. 6. Analysis of methylation kinetics of $Mmnt_2^{2-}$ complexes. $Mmnt_2^{2-}$ concentrations of Figs. 2–4, measured at CH_3I concentration = $5.95 \cdot 10^{-1}$ mol·l^{-1}.

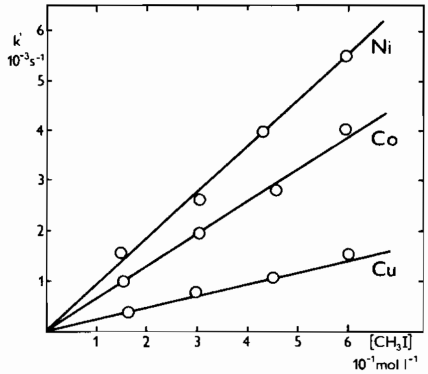

Fig. 7. Dependence of pseudo-1st-order rate constant k' on CH_3I concentration.

ing that the reaction is also of first order with respect to CH_3I. The slope of this plot is equal to rate constant k. The measured values of rate constants, k, are given in Table I. The rate-law corresponding to the methylation of $Mmnt_2^{2-}$ (M = Co, Ni, Cu) complexes is thus given by eqn. 2:

$$\frac{dx}{dt} = k \cdot [Mmnt_2^{2-}] \cdot [CH_3I] \qquad (2)$$

This rate-law indicates that the rate determining step is the methylation of one, most probably the first sulphur donor atom:

$$Mmnt_2^{2-} + CH_3I \rightarrow [M(Memnt)mnt]^- + I^- \qquad (3)$$

This reaction is followed by much faster methylation of further sulphur atoms and by fast complex decomposition.

Methylation of $Znmnt_2^{2-}$ complex proceeds *via* a much more complicated reaction mechanism (Fig. 5). The absorbance decreases in first stages of the reaction with time, passes through a minimum and increases to the value A_∞, which depends on concentration of CH_3I.

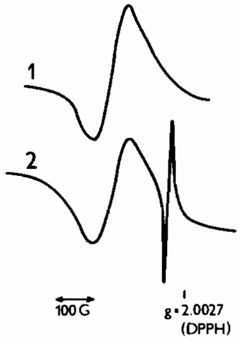

Fig. 8. EPR spectrum of the reaction intermediate in reaction of $Rhmnt_2^{2-}$ with CH_3I. 1: 10^{-3} mol·l^{-1} $[Bu_4N]_2$-$[Rhmnt_2]$; 2: 315 seconds after addition of $4 \cdot 10^{-4}$ mol·l^{-1} CH_3I.

These complicated experimental results may be explained by a combination of following and parallel reactions. The rate constant of the rate-determining step was estimated to be of the order 10^{-3}–10^{-2} l mol^{-1} s^{-1}. The detailed mechanism was not studied.

Methylation of $Mmnt_2^-$ (Co, Ni, Cu) Complexes

Absorption spectra in UV or visible region of solutions containing $Mmnt_2^-$ (M = Co, Ni, Cu)* complexes with CH_3I in molar concentration more than 300-times greater than that of the complex do not change appreciably for several hours. (The methylation of corresponding dianions would be completed under the same conditions in less than 15 min.) In the course of longer time periods, solutions slowly decompose, as is manifested by decrease of all absorption bands. However, even this decomposition reaction is very slow – about 25% over 24 hours in all cases. The spectroscopic picture of the slow decomposition of $Mmnt_2^-$–CH_3I solutions is qualitatively the same, or rather little faster, as that of the spontaneous decomposition of pure solutions of $Mmnt_2^-$ complexes. The decomposition of $Mmnt_2^-$ complexes in the presence of CH_3I cannot be therefore looked upon as methylation reaction analogous to that of $Mmnt_2^{2-}$ complexes. It is thus concluded that *$Mmnt_2^-$ complexes (M = Co, Ni, Cu) cannot be methylated by CH_3I* in a way analogous to that of corresponding $Mmnt_2^{2-}$ complexes.

Reaction of $Rhmnt_2^{2-}$ with CH_3I

$Rhmnt_2^{2-}$ complex reacts with CH_3I by different mechanism than other $Mmnt_2^{2-}$ complexes. This reaction is now under detailed investigation. Here only fundamental results will be reported to make

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*$Comnt_2^-$ complex is, in fact, a dimeric species $[Comnt_2]_2^{2-}$ in the solution being partially dissociated to the monomers [23].

the comparison with other studied complexes possible.

The reaction of Rhmnt$_2^{2-}$ with CH_3I proceeds much faster than methylation of other Mmnt$_2^{2-}$ species. The green colour of solution of Rhmnt$_2^{2-}$ turns immediately brown-red after mixing with CH_3I. This reaction does produce neither Me$_2$mnt nor any other species containing S–CH_3 bond as was proved by ^{1}H NMR spectra. The final product of this reaction is, most probably, identical with the product of simple oxidation of Rhmnt$_2^{2-}$, *i.e.* it is a mixture of [Rhmnt$_2$]$_n^{n-}$ polymeric species [22].

The reaction of Rhmnt$_2^{2-}$ with CH_3I was studied also by following the EPR spectra of the reaction mixture with concentration of CH_3I lower than that of Rhmnt$_2^{2-}$ complex. Under these conditions, decrease of the EPR signal of Rhmnt$_2^{2-}$ (g = 2.129, ΔH_{pp} = 95 G) and appearance of a new singlet signal (g = 2.029, ΔH_{pp} = 11 G) was observed (Fig. 8). Intensity of the new signal at g = 2.029 changes with time: it passes through a maximum and afterwards (slowly) limits to zero. This time-dependence points to the conclusion, that the observed EPR signal is due to a reaction intermediate. Oxidation of Rhmnt$_2^{2-}$ by simple oxidating agents (I_2, tetracyanoethylene, O_2) products identical EPR-characterized intermediate, its EPR paramaters being independent upon the nature of the solvent used (THF, dimethylformamide) and of the oxidating agents [12, 13]. This paramagnetic intermediate of oxidation of Rhmnt$_2^{2-}$ is, probably, a dimeric species [Rhmnt$_2$]$_2^{3-}$ [13]. However, the reaction of Rhmnt$_2^{2-}$ with simple oxidating agents proceeds faster than its reaction with CH_3I, as is manifested by the rate of decrease of the Rhmnt$_2^{2-}$ EPR signal.

Summarizing these results, it may be concluded that Rhmnt$_2^{2-}$ reacts with CH_3I much faster than other Mmnt$_2^{2-}$ complexes. This reaction *is, however, not a methylation of sulphur donor atoms.* It is, most probably, simple oxidation reaction producing polymeric species [Rhmnt$_2$]$_n^{n-}$ with a rather complicated mechanism.

Discussion

Dianionic bis(maleonitriledithiolato) complexes, Mmnt$_2^{2-}$ (M = Co, Ni, Cu), were found, contrary to previous results [1, 2], to be methylated with CH_3I on sulphur donor atoms. Since all these complexes may be described [10–14] as complexes of formally dianionic ligands, mnt^{2-}, it may be concluded, that the occurrence of S-donor atom methylation is a *general indication of the dianionic nature of coordinated dithiolene ligand $S_2C_2R_2^{2-}$*, regardless of the nature of ligand substituent R. The principal effect of the electron withdrawing substituent (R = CN) is the weakening of the M–S bond in the methylated product resulting in its rapid dissociation, in contrast to other methylated dithiolato ligands, *e.g.* $Me_2S_2C_2Ph_2$ [1–4].

The reactions of Mmnt$_2^{2-}$ (M = Co, Ni, Cu) with CH_3I are analogous with identical rate determining step (eqn. 2). Znmnt$_2^{2-}$ complex reacts in an analogous way, but with a more complicated mechanism. As the product of this reaction is identical with that of other Mmnt$_2^{2-}$ complexes and as estimated rate constant does not drastically differ from that of other methylation reactions studied, we may conclude that also the bonding and nature of mnt-ligands in all these complexes is similar. This conclusion is supported by electrochemical [11, 13] and IR data [24].

It is seen (Table I) that even the rate constants of methylation of different Mmnt$_2^{2-}$ complexes depend only slightly on the nature of the central metal atom. The parallelity of the rate constant with total charge on sulphur atoms (q_s) is evident: the q_s-values in Comnt$_2^{2-}$ and Nimnt$_2^{2-}$ complexes are rather close, as are the values of corresponding rate constants. The decrease of the rate constant in the case of Cu-complex parallels the estimated decrease of q_s.

The remarkable unreactivity of monoanions Mmnt$_2^-$ (M = Co, Ni, Cu) towards CH_3I may be also correlated with the strong decrease of q_s when going from dianions Mmnt$_2^{2-}$ to monoanions Mmnt$_2^-$ (see Table I). This change of methylation reactivity with the change of oxidation state of the Mmnt$_2^{n-}$ species points to the conclusion, that the nature of ligands in monoanions Mmnt$_2^-$ is different as compared with that in dianions Mmnt$_2^{2-}$: in Mmnt$_2^-$ the dianionic nature of the ligand is not preserved, the change in the number of electrons is obviously localized in the ligand-based molecular orbitals. As these orbitals are strongly delocalized, it is therefore more appropriate to treat both dithiolene ligands as a 'ligand cluster' and to describe the monoanionic species Mmnt$_2^-$ (M = Co, Ni, Cu) formally as complexes of M(II) with coordinated 'mnt$_2^{3-}$ ligand cluster'. This description agrees fully with electrochemical results [10, 11, 13].

Comparison of all these results leads to some implications about localization of highest occupied molecular orbitals (HOMO) in the complexes studied (The uppermost molecular orbitals are depicted in Fig. 9**). The mnt-ligands in planar complexes may be looked-on as dianionic (or as mnt$_2^{4-}$ ligand cluster) only if the localization of b_{1u}, b_{2g} and/or b_{2g}^* molecular orbitals makes parent ligand orbitals fully occupied. As the b_{1u} orbital is in all studied complexes occupied by two electrons and predominantly ligand-

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**For qualitative MO-schemes of planar dithiolene complexes see refs. [3, 23, 25] and ref. [14] for detailed analysis of uppermost MOs. Construction of MOs is explained in ref. [25].

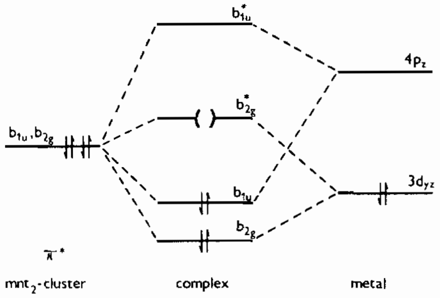

Fig. 9. Simplified scheme of uppermost molecular orbitals of Mmnt$_2$-complexes (M = Co, Ni, Cu). b_{2g}-orbital is singly occupied in Comnt$_2^{2-}$ and Nimnt$_2$ doubly occupied in Nimnt$_2^{2-}$ and Cumnt$_2$ complexes.

localized, our further discussion concerns only b_{2g} and b_{2g}^* orbitals. The b_{2g}^* molecular orbital is HOMO both in Mmnt$_2^{2-}$ (M = Co, Ni) and Mmnt$_2^-$ (M = Ni, Cu) complexes.

The course of the methylation reaction points to the conclusion that there are considerable differencies in the localization of these orbitals in the pairs of formally isoelectronic complexes Comnt$_2^{2-}$–Nimnt$_2^-$ and Nimnt$_2^{2-}$–Cumnt$_2^-$: The singly occupied b_{2g}^* antibonding orbital has to be predominantly metal-localized in Comnt$_2^{2-}$ complex. Corresponding predominantly ligand-localized b_{2g} bonding orbital is then doubly occupied leading to dianionic ligand character (see Fig. 9). On the other hand, in Nimnt$_2^-$-complex, the singly-occupied b_{2g}^* orbital has to be predominantly ligand-localized (and b_{2g} thus metal-localized) to get the electron-deficient ligand cluster, mnt$_2^{3-}$, whose formal existence in the Nimnt$_2^-$ molecule was deduced from its apparent unreactivity towards CH_3I.

This picture, using only the uppermost orbitals is, of course, an oversimplification, the charge and reactivity of sulphur atoms being influenced by the localization of other molecular orbitals also. However, the uppermost orbitals seem to play the decisive role.

The reactivity of Rhmnt$_2^{2-}$ considerably differs from that of other Mmnt$_2^{2-}$ complexes. The rhodium complex is rapidly oxidized by CH_3I to [Rhmnt$_2$]$_n^{n-}$ species, in spite of the fact that mnt-ligands in this complex have also dianionic character as follows from electrochemical data [10–13] and from the frequencies of ligand vibrations which are very similar in Rhmnt$_2^{2-}$ and other Mmnt$_2^{2-}$ complexes. The mnt^{2-} ligands in Rhmnt$_2^{2-}$ complex should therefore be potentially able to react with CH_3I in usual way, *i.e.* methylation at nucleophilic S-donor atoms would be expected. However, the experimental data show that a different mechanism operates. It may be assumed, that the primary interaction between the complex and CH_3I takes place at the metal center. This seems to be connected with the different nature of HOMO in the rhodium complex (which is a metal d_{z^2}-based a_{1g} MO [14]) and with its greater tendency towards oxidation reactions due to the formation of stable polymeric products.

The comparison of the methylation reactions of dithiolene complexes having several reactivity centers (Rhmnt$_2^{2-}$ or substituted dithiolene complexes [7–9]) may therefore help to elucidate the reactivity patterns of individual centers of reactivity in the complex molecule.

Conclusions

Mmnt$_2^{2-}$ complexes (M = Co, Ni, Cu, Zn) were found, contrary to previous results [1–3], to react with CH_3I producing free Me$_2$mnt species in THF. The most nucleophilic center of these complexes are thus sulphur donor atoms. Existence of this reaction proves that methylation of sulphur donor atoms may be regarded as a general indication of the dianionic nature of the dithiolene ligand regardless the ligand substitutents. This reaction depends strongly upon the electron density localized on mnt-ligands as follows from the great decrease of reactivity when going from dianions Mmnt$_2^{2-}$ to corresponding monoanions, Mmnt$_2^-$. However, the rate constant is rather insensitive to changes of the central metal atom (M = Co, Ni, Cu, Zn) suggesting a similar type of bonding in all these complexes.

As the methylation reaction reflects principal changes of the electron distribution in the complex molecule, its occurrence, rate and mechanism may serve as an unseful tool to draw qualitative conclusions on relative ordering, localization and occupancy of uppermost molecular orbitals of the complex molecule, and to elucidate the nature of reactivity centers in more complicated dithiolene complexes.

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