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Electrocatalytic CO_2 reduction in methanol catalyzed by mono-, di-, and electropolymerized phthalocyanine complexes

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The electroreduction of CO_2 was studied in methanol in the presence of mono- and diphthalocyanine complexes and phthalocyanine films prepared by electrochemical anodic polymerization. Methyl formate is the main reaction product of the reaction catalyzed by the mono- and diphthalocyanine complexes of rare-earth metals. Copper 2,9,16,23-tetra-*tert*-butylphthalocyanine allows the transformation of CO_2 into methane in ~30% yield. In the presence of both electropolymerized and graphite electrode-supported copper 2,9,16,23-tetraaminophthalocyanine, CO and methyl formate are the main reaction products.

Key words: electrocatalysis, diphthalocyanine complexes, carbon dioxide, electropolymerized films, semiempirical quantum-chemical calculations.

Monophthalocyanine complexes are known[1—5] to catalyze electrochemical CO_2 reduction in protic media to form CO,[6—18] HCOOH,[6,7,17—19] and CH_4.[17,18]

$$CO_2 + 2e + 2H^+ \longrightarrow HCOOH$$

$$CO_2 + 2e + 2H^+ \longrightarrow CO + H_2O$$

$$CO_2 + 8e + 8H^+ \longrightarrow CH_4 + 2H_2O$$

Methanol can also be formed in the six-electron reduction of CO_2 in water.[19] The CO to CH_4 ratio is determined to a great extent by the metal nature. In the case of VIII Group transition metals, *viz.*, Co, Ni, Fe, and Pd, the main reaction product is CO.[6,9—13,17—20] Electrolysis of CO_2 in the presence of Sn, Pb, In, Zn, and Al phthalocyanines produces[6,17,18] mainly HCOOH, and almost equal amounts of HCOOH and CO are formed in the case of Zn. The highest selectivity to HCOOH is achieved with the In and Sn complexes. In the presence of Cu, Ga, and Ti phthalocyanines, methane is predominantly formed, although in a low yield.[17,18] Unlike the metal complexes, phthalocyanine itself is low efficient in CO_2 reduction.[21]

The electrocatalytic properties of diphthalocyanine complexes are poorly studied. We have previously[22] studied the reaction of CO_2 with epoxides producing alkylenecarbonates. The reaction is catalyzed by electrochemically reduced forms of the mono- and diphthalocyanine complexes of transition and rare-earth metals. In this case, the composition of the reaction products is independent of the nature of the phthalocyanine complex. The advantage of using diphthalocyanines is low cathodic overvoltages of the process performing.

Diphthalocyanine complexes were not studied earlier as electrocatalysts for CO_2 reduction in protic media. The purpose of this work is a comparative study of the catalytic effect of various mono- and diphthalocyanine complexes and phthalocyanine films prepared by the electrochemical anodic polymerization of the tetraamino-substituted monophthalocyanine complexes in carbon dioxide electroreduction in methanol.

Experimental

The phthalocyanine complexes were synthesized according to previously published procedures.[23—25]

The electrocatalytic CO_2 reduction was carried out in MeOH in the presence of 0.05 *M* Bu_4NBF_4 in a 10-mL two-compartment electrochemical cell. A graphite rod 5 mm in diameter (graphite of the "MG" trade mark, specially pure grade), on which the studied phthalocyanine complex was supported, was used as a working electrode. A Pt plate served as an auxiliary electrode, and Ag/AgCl/KCl was a reference electrode. The potentials were corrected for the ohmic drops. Electrolysis was performed in the potentiostatic regime using a P-5848 potentiostat with a correction for the ohmic drops in a solution.

The catalyst was loaded by the impregnation of the electrode with a solution of the complex ($5 \cdot 10^{-4}$ mol L^{-1}) in CH_2Cl_2

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followed by drying with a warm air flow or by precipitation from a DMF solution with ether (for poorly soluble complexes).

In several cases, the phthalocyanine complex was deposited by oxidative electrochemical polymerization. Copper 4,9,16,23-tetraaminophthalocyanine (^{NH_2}PcCu), which was synthesized in two stages according to a previously described procedure,**[23]** was used as the initial monomer for electropolymerization. A 0.1 *M* solution of Bu_4NBF_4 in DMF saturated with ^{NH_2}PcCu (~$5 \cdot 10^{-4}$ mol L^{-1}) was used for electropolymerization. The films were deposited in the potential cycling regime in −1.0—+0.8 V interval with a scan rate of 50 mV s^{-1} and a storage for 10 s at –0.1 V (*vs.* aqueous saturated Ag/AgCl/KCl). The number of cycles during electrochemical deposition was 20—40.

Before electrolysis argon was bubbled through a methanol solution for 10 min to remove dioxygen traces, and then a solution was saturated with CO_2 for 15 min. Gases evolved from the cell were collected in a gas burette equipped with a rubber septa for sampling a gas mixture during electrolysis. An excess of unreacted CO_2 was absorbed by passing a gas mixture through an aqueous 1 *M* solution of KOH.

Gaseous products were analyzed on a Chrom-5 chromatograph (thermal conductivity detector, column (2 m) packed with molecular sieves 5 A (40/60 mesh)). Argon was used as the carrier gas. A solution obtained in electrolysis was analyzed on the same chromatograph with a flame-ionization detector and a column (2 m) packed with 10% Carbowax 20 M on Chromosorb W HP (80/100 mesh). The composition of the reaction products was determined using the absolute calibration method.

Quantum-chemical calculations were performed using the semiempirical SCF PM3 method extended by the inclusion of the parameters for all transition metals of the first row and some metals of the second and third rows. This method (PM3(tm)) is in the HyperChem 6.01 program package (HyperCube Inc., FL, USA). The geometry of molecules was optimized with the established convergence gradient ≤10 cal $Å^{-1}$ mol^{-1}.

Results and Discussion

Electrocatalytic CO_2 reduction in the presence of the phthalocyanine complexes was carried out in MeOH because the solubility of CO_2 in it is much higher than in H_2O (4.6 and 1.07 mL mL^{-1}, respectively).**[26]** In addition, the acid dissociation constant for MeOH in MeOH (>30) is much lower than that for water (15.7) and, hence, competitive H_2 evolution in MeOH occurs to much lower extent.

Copper 2,9,16,23-tetra-*tert*-butylphthalocyanine ($^{Bu^t}$PcCu), copper 2,9,16,23-tetraaminophthalocyanine (^{NH_2}PcCu), lutetium monophthalocyanine (PcLuOAc), lutetium (Pc_2Lu) and dysprosium diphthalocyanines (Pc_2Dy), lutetium 2,3,9,10,16,17,23,24,2´,3´,9´,10´,16´,17´,23´,24´-hexadecapentoxydiphthalocyanine ($^{C_5H_{11}O}Pc_2Lu$), and electropolymerized tetraamino-substituted copper monophthalocyanine (poly-^{NH_2}PcCu) were used as catalysts.

In the presence of all these complexes, the catalytic increase in the current is observed when CO_2 is passed through a solution, which is seen from a comparison of the voltammetric curves obtained in argon and CO_2 at potentials more cathodic than −1.2 V. As an example, Fig. 1 presents the voltammetric curves obtained for $^{Bu^t}$PcCu, electropolymerized ^{NH_2}PcCu, and Pc_2Lu. These data indicate that the complexes under study catalyze electrochemical CO_2 reduction.

The results of GLC analysis of the reaction products formed in electrolysis (Table 1) show an increase in the yield of methane from ~20 to 30% when the

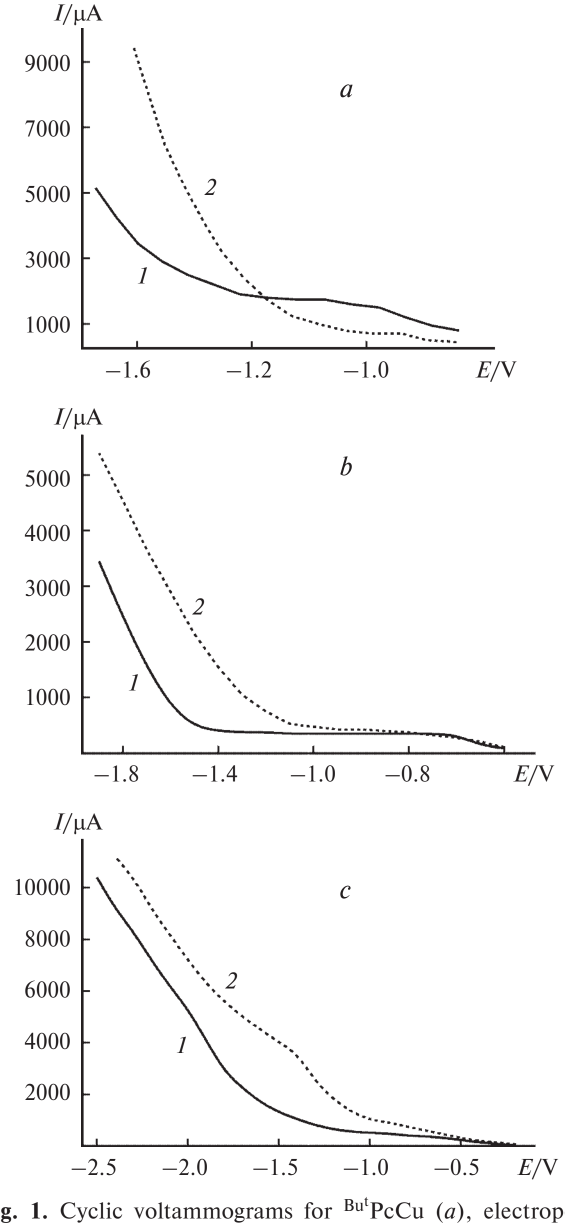

Fig. 1. Cyclic voltammograms for $^{Bu^t}$PcCu (*a*), electropolymerized ^{NH_2}PcCu (*b*), and Pc_2Lu (*c*) (graphite, MeOH, 0.05 *M* $Bu^n{}_4NBF_4$, *vs.* Ag/AgCl/KCl) in argon (*1*) and CO_2 (*2*).

Table 1. Current efficiencies for the products of electrocatalytic CO_2 reduction in the presence of phthalocyanine complexes[a]

Complex	$-E$/V[b]	Current efficiency (%)			
		CO	CH_4	HCOOMe	H_2
$^{\mathrm{Bu^t}}$PcCu	1.8	0.5—1.5	15—20	35—40	25—35
	2.5	0.5—1.5	22—32	30—40	35—45
PcLuOAc	2.5	8—10	3—5	40—45	50—55
Pc_2Lu	1.2	10—15	0	32—40	25—30
	2.5	8—10	0.5—1.5	45—50	45—50
Pc_2Dy	2.5	8—10	0.7—2.0	45—50	45—50
$^{\mathrm{C_5H_{11}O}}Pc_2Lu$	2.5	4—6	1—3	25—30	55—60
$^{\mathrm{NH_2}}$PcCu	1.6	2—3	0—0.5	45—55	40—50
	2.1	5—9	0—0.5	30—40	50—60
$^{\mathrm{NH_2}}$PcCu [c]	1.1	3—5	0	50—60	23—33
	1.5	53—65	1—2	25—30	23—33
	1.8	30—35	2—4	30—35	30—35
	2.0	29—33	2—4	20—25	37—45

[a] Experimental conditions: MeOH, 0.1% solution of $KHCO_3$, 0.05 *M* Bu_4NBF_4, 20 °C, averaging over experimental points (Fig. 2) during an electrolysis time of 2 h.
[b] *Vs.* Ag/AgCl/KCl.
[c] Electropolymerized sample.

cathodic potential increases from −1.8 to −2.5 V (*vs.* Ag/AgCl/KCl) for catalysis by the $^{\mathrm{NH_2}}$PcCu complex. In the presence of Pc_2Lu, for the cathodic potential bias of electrolysis, the yield of CO decreases and that of methyl formate increases. In the case of electropolymerized $^{\mathrm{NH_2}}$PcCu, the maximum yield of CO is found at −1.5 V because at higher cathodic potentials the polymeric film is partially destroyed and its conductivity and, correspondingly, catalytic activity decrease.

Table 1 contains the results of electrolysis for the total electrolysis time (2 h). The time dependences of the yields of the products were also studied. The composition of the gas products was analyzed at an interval of 30 min. These results indicate that the relative amounts of the gaseous products change during the reaction (Fig. 2). The gas mixture obtained in the first 30 min of electrolysis does not virtually contain methane. Significant amounts of CO begin to appear later, 60—90 min after the beginning of the process. This is explained by rather high solubility of methane and CO in the reaction medium (MeOH) and in water (above which the gas mixture is collected)*. Therefore, it is more correct to use the averaged current efficiences measured within the time from the appearance of the gaseous products in the gas phase to the beginning of gradual catalyst deactivation (2.0—2.5 h). Thus calculated current efficiencies for the gaseous products are presented in Table 2.

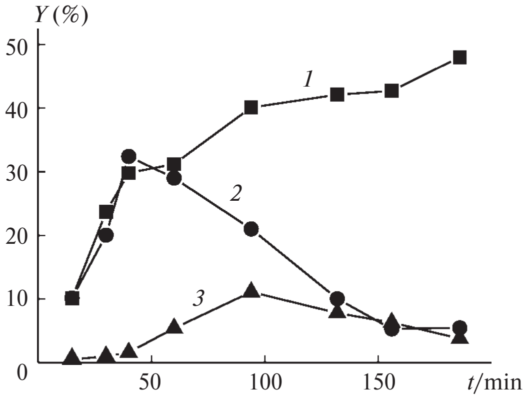

Fig. 2. Plot of the current efficiency (Y) for H_2 (*1*), CH_4 (*2*), and CO (*3*) *vs.* electrolysis time (*t*) for gaseous products of electrocatalytic CO_2 reduction in the presence of $^{\mathrm{Bu^t}}$PcCu (MeOH, 0.05 *M* $KHCO_3$).

Table 2. Maximum current efficiency for gaseous products of electrocatalytic CO_2 reduction in the presence of phthalocyanine complexes[a]

Complex	$-E$/V[b]	Current efficiency (%)		
		CO	CH_4	H_2
$^{\mathrm{Bu^t}}$PcCu	2.5	2.5—3.5	29—35	35—45
PcLuOAc	2.5	15—17	3—4	50—55
Pc_2Lu	1.2	30—35	0	25—30
	2.5	15—17	0.5—1.5	45—50
Pc_2Dy	2.5	15—17	0.7—2.0	45—50
$^{\mathrm{C_5H_{11}O}}Pc_2Lu$	2.5	6—8	2—3	55—65
$^{\mathrm{NH_2}}$PcCu	2.1	7—10	0—0.5	50—60
$^{\mathrm{NH_2}}$PcCu [c]	1.5	75—85	2—3	20—30

[a] Experimental conditions: MeOH, 0.1% solution of $KHCO_3$, 0.05 *M* Bu_4NBF_4, 20 °C.
[b] *Vs.* Ag/AgCl/KCl.
[c] Electropolymerized sample.

As can be seen in Tables 1 and 2, the composition of the electrolysis products strongly depends on both its potential and the structure of phthalocyanine complex (substituent in the macrocyclic ligand).

Although many works were devoted to the electrocatalytic reduction of CO_2 in protic media, its multistep mechanism is not understood. A few data on the mechanism of CO_2 electroreduction catalyzed by the phthalocyanine complexes in protic media concern mainly PcCo.[10,11,13] Based on our results and published data, we proposed a probable scheme of consecutive stages of electrocatalytic CO_2 reduction to MeOH involving metal phthalocyanines (Scheme 1).

This sequence includes electron transfer from the electrode to catalyst, inner-sphere electron transfer from the catalyst to the axial ligand bound to the metal, and the protonation and elimination of the reaction products.

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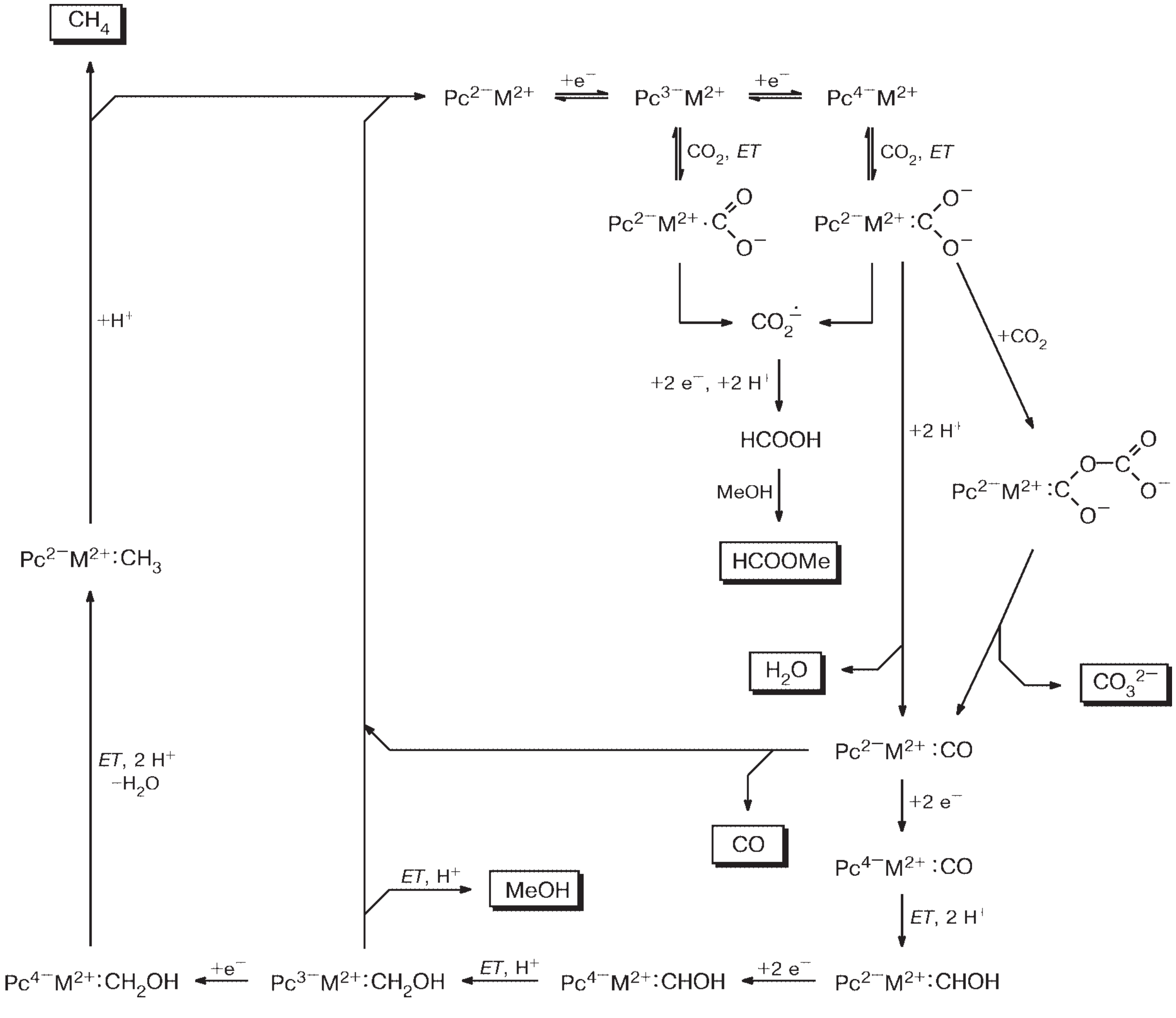
* Solubility of CH_4 in MeOH [27] and in water[28] is 60 mL per 100 mL (20 °C), and that of CO in water is 20 mL per 100 mL (20 °C).[28]

Scheme 1



ET is electron transfer

Scheme 1 presents the catalytic cycle for copper phthalocyanine because precisely this complex makes it possible to perform the deepest CO_2 reduction (to CH_4).

According to this scheme, the extent of CO_2 reduction and, hence, the composition of the reaction products are determined by the reduction ability of the anionic form of the complex and the stability of intermediate adducts. The latter determines either the further development of the catalytic cycle to form deeper reduction products or the formation of HCOOH or CO and, thus, shortening the cycle.

The obtained experimental data (see Tables 1 and 2) indicate that for the substituted copper monophthalocyanine complexes the products composition of electrocatalytic CO_2 reduction strongly depends on the nature of the substituent in the phthalocyanine ring. The use of ${}^{\mathrm{Bu^t}}$PcCu as catalyst makes it possible to produce CH_4 with 30% current efficiency. The reduced form of ${}^{\mathrm{Bu^t}}$PcCu is a strong reducing agent, which in the first stage transforms CO_2 into the radical anion ($CO_2{}^{\bullet -}$). Some portion of the radical anion transforms into HCOOH, whereas another $CO_2{}^{\bullet -}$ portion coordinates with the paramagnetic Cu atom in the reduced form of the complex. Then, through a series of subsequent stages, $CO_2{}^{\bullet -}$ transforms into CO (see Scheme 1). However, the adduct (CO precursor, see Scheme 1) is sufficiently stable because CO can form a strong σ-bond with the d_{z^2}-orbital of the Cu atom (see below) and, therefore, the CO yield is low and the catalytic cycle develops further to form CH_4.

The methane yield is very low in the case of catalysis by the ${}^{\mathrm{NH_2}}$PcCu complex. This can be related to the fact that the amino groups with the strong electron-donor effect substantially enhance the electron density on the phthalocyanine ring and Cu atom. This enhances the level of its d_{z^2}-orbital and decreases, most likely, the efficiency of the interaction of this orbital with the CO orbitals, thus impeding its coordination and deeper reduction.

The coordination of $CO_2^{\bullet -}$ with the reduced form of the ^{NH_2}PcCu complex is also less favorable than that in the case of $^{Bu^t}$PcCu. Therefore, methyl formate formation is the predominant process in the first branching point in the scheme.

It is of interest that CO is formed as the main product when electropolymerized copper tetraaminophthalocyanine is used as catalyst. We cannot explain this fact.

Our results and the published data[18] show that the high methane yield is reached when CO_2 is reduced in the presence of copper phthalocyanines (PcCu and $^{Bu^t}$PcCu), while the methane yield is very low with phthalocyanines of other transition metals (except Ti). The reason for such a distinction in behavior of different metal complexes is of theoretical interest, and several publications are devoted to this problem. For example, the catalytic activity of neutral (unreduced) phthalocyanines can be related to the energy of frontier orbitals of the complex. It was shown[29] that the catalytic activity of monophthalocyanine complexes correlates with their capability of coordinating an additional axial ligand to the metal atom, which depends on the difference between energies of the d-orbitals of the metal phthalocyanine and frontier orbitals of the coordinating ligand.

The reduced $[PcM]^{n-}$ complex has the high-energy HOMO formed from the LUMO of the initial neutral complex and, according to the calculations,[18] mainly localized on the N atoms of the phthalocyanine ligand. Therefore, $(PcM)^{n-}$ is a strong reducing agent, and it reduces CO_2 to CO.[18] If CO is weakly bound to the metal of the complex, its considerable portion is evolved, and the final reaction products contain much CO. This situation is observed when the metal is bound to CO by its $d_{xz}(d_{yz})$-orbitals, and the d_{z^2}-orbital is not involved in the binding (for example, if it is already doubly occupied). Then the back donation with the π^*-orbital of CO should involve mainly the d_{z^2}-orbital, *i.e.*, it will be weak.

If the electron pair of the CO molecule is bound to the metal by the σ-M—C bond, *i.e.*, by the $(n)d_{z^2}$-orbital involving the $(n + 1)p_z$- and $(n + 1)$s-orbitals, its further catalytic reduction to CH_4 is possible on the electrode surface or in a solution.[18]

However, if the d-levels of the metal are low-lying (Sn, Pb, In, Zn, Al, and others), they are not involved in the ligand binding. In this case, the binding occurs only through the s- and p-orbitals. The LUMO of the initial PcM is less localized, *i.e.*, it is higher in energy compared to the first case. Then the electron transfer to this LUMO during electrochemical reduction enhances its energy to a lower extent, *i.e.*, $(PcM)^{n-}$ will be a weaker reducing agent. It is quite possible that CO_2 is reduced not to CO but only to the $CO_2^{\bullet -}$ radical anion, and the latter produces formic acid.[18]

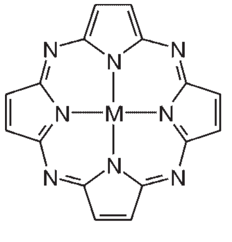
The metal d- and f-levels in monophthalocyanines of rare-earth metals are very low in energy and, hence, do not participate in bonding.[30] In this case, the catalytic process involves the orbitals of the phthalocyanine ring and produces formic acid as the main reaction product because the reduced form of PcLuOAc is a rather weak reducing agent.

In the case of diphthalocyanine complexes of rare-earth metals, the orbitals of the phthalocyanine rings and the metal ion are highly separated in energy and, hence, the interaction between them is negligible.[30] The interaction of two phthalocyanine rings somewhat decreases the energy of the complex LUMO.[30] Therefore, the reduced form of diphthalocyanine is a weaker reducing agent compared to monophthalocyanine. As our semi-empirical calculations showed,[22] in the case of diphthalocyanine complexes the coordination of the CO_2 or CO molecule to the metal atom is strongly impeded due to steric reasons. Therefore, in this case, electrocatalytic CO_2 reduction produces no substantial amounts of methane but gives formic acid and CO in a ~5 : 1 ratio of current efficiencies.

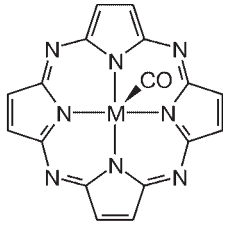
In the diphthalocyanine complexes coordination with the metal is absent. Instead, the peripheral N atom of the phthalocyanine ring is probably involved in coordination,[22] enabling the formation of both methyl formate and CO (see Scheme 1).

In the case of lutetium diphthalocyanine containing bulky substituents (pentoxy groups) in the phthalocyanine rings, the yields of the products of CO_2 reduction are much lower than those for nonsubstituted diphthalocyanines, and hydrogen evolution is the main process in this case. Perhaps, this is related only to steric hindrances to the electron transfer from the reduced form of phthalocyanine to the CO_2 molecule.

To confirm the conclusions about the influence of the metal nature in the phthalocyanine complex on the composition of the products of electrocatalytic CO_2 reduction, we performed comparative quantum-chemical calculations of the Co, Ni, Cu, and Zn complexes (**1a—d**) and their adducts with CO (**2a—d**). Tetraazaporphyrins were used instead of phthalocyanines to simplify and shorten the time of calculations.



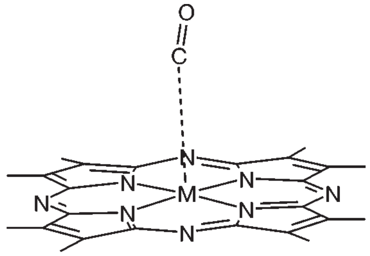
1a—d



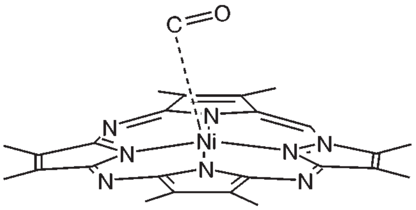
2a—d

M = Co (**a**), Ni (**b**), Cu (**c**), Zn (**d**)

The neutral complexes and their anions (monoreduced forms) and dianions (doubly reduced forms) were calculated. In all cases, except the Ni complexes, in the LM—CO molecule (L is the ligand) the axial C—O group was perpendicular to the ligand plane and the metal atom was slightly shifted from this plane toward CO. However, according to the results of calculation of the geometry of LNi—CO, the Ni—C—O angle was 94°, and this arrangement of the C—O ligand retained in the mono- and dianion.

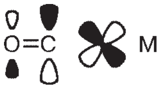


M = Fe, Co, Cu, Zn



Some structural data for the Co, Ni, Cu, and Zn complexes and for the free CO molecule and its mono and doubly reduced forms are presented in Table 3. The calculations allow the following conclusions: (1) when the negative charge of the complex increases from 0 to –1 and then to –2, the M—C bond in the Co and Ni complexes shortens and that in the Cu and Zn complexes elongates; (2) the same charge change slightly elongates the C—O bond for all compounds of Co, Ni, Cu and Zn; and (3) the reduction of free CO much more elongates the C—O bond than that in the case of the LM—CO complexes.

These data can be explained under assumption that in the Co and Ni complexes the back donation, *i.e.*, π^*(CO)—$d_{xz(yz)}$(M) interaction (**A**), plays the main role in the Co and Ni complexes, whereas in the Cu and Zn complexes the normal binding of CO as a Lewis acid, *i.e.*, n(CO)—$d_{z^2}(p_z,s)$(M) interaction (**B**), is of first importance.



A

B

Table 3. Calculated by the PM3(tm) method the M—C and C—O bond lengths (*d*), heats of formation (ΔH_f) for LM[a] and LM—CO, differences of the heats of formation for these complexes in the neutral, mono-, and direduced forms, the C=O bond length and heats of formation for carbon monoxide and its two reduced forms

M	Charge	*d*/Å		ΔH_f/kcal mol^{-1}		$\Delta\Delta H_f$[b]
		M—C	C—O	LM	LM—CO	
Co	0	1.817	1.151	–23.94	–168.55	–164
	–1	1.729	1.157	–114.77	–248.57	–136
	–2	1.715	1.162	–90.12	–236.45	90
Ni	0	2.061	1.162	6.53	–46.05	–72
	–1	2.033	1.166	5.44	–120.82	–127
	–2	2.016	1.172	–31.41	–109.51	158
Cu	0	2.139	1.140	84.32	42.55	–62
	–1	2.148	1.144	11.59	–26.79	–40
	–2	2.152	1.147	26.07	–236.45	–26
Zn	0	2.171	1.133	239.8	198.12	–62
	–1	2.188	1.136	162.77	125.33	–39
	–2	2.211	1.140	175.5	142.0	203
C=O[c]	0	—	1.134	–19.76	—	—
	–1	—	1.190	–2.52	—	—
	–2	—	1.257	236.21	—	—

[a] L is the tetraazaporphyrin dianion.

[b] $\Delta\Delta H_f$ (kcal mol^{-1}) = $\Delta H_f(\mathrm{LM—CO})^{n-} - \Delta H_f(\mathrm{LM})^{n-} - \Delta H_f(\mathrm{CO})^{n-}$ (n = 0, 1, 2).

[c] Calculated C=O bond lengths and heats of formation for the CO molecule and its radical anion and dianion.

Even if in the series [LM—CO]^0, [LM—CO]$^{1-}$, and [LM—CO]$^{2-}$ the electron density changes mainly on the ligand, the population of the metal d-levels still increases. Then the back donation enhances, and the Lewis binding weakens; if the former is more important, the C—M bond should shorten (as in the case of Co and Ni), and if the Lewis binding is more significant, this bond should elongate (Cu and Zn).

This assumption is confirmed by the data of CO adsorption on the metal surface. The spectroscopic studies (UPS, EEIS, IRAS)[31] revealed a correlation between the electronic and vibrational properties of CO chemisorbed on the metal surface. The authors[31] concluded that strong CO chemisorption needs electron transfer from the Lewis n(σ)-orbital of CO to the vacant d-, s-, and p-orbitals of the metal and this transfer is accompanied by the back donation of electrons from the metal to the CO π^*-orbital. This bonding is more significant for CO adsorption on VIII Group metals, and adsorption on Cu is mainly a result of the direct donation of the CO n(σ)-electrons to the metal. This is confirmed by measurements of the electron work function. All VIII Group metals are characterized by an increase in the electron work function upon CO adsorption, whereas Cu is characterized by its decrease. The results obtained indicate that in the case of Cu the charge is transferred from CO to the metal, and for VIII Group metals, on the contrary, the transfer occurs from the metal to CO.[32] In the case of Cu, the influence of the adsorbed CO molecule on the binding of the newly coming CO molecule is greater than that for adsorption on VIII Group metals. Electron donation on transition metals is strongly compensated by back donation, and for Cu this compensation is much weaker. Therefore, with increasing the coverage of the Cu surface with CO molecules when the counteraction to direct donation is enhanced, thus decreasing the ν(CO) frequency of stretching vibrations. In the case of VIII Group metals with a high contribution of back donation, this effect is insignificant.

The slight increase in the C—O bond length with an increase in the negative charge of the complex is probably associated with the enhancement of back donation due to the greater donating ability of the d-orbitals in the negatively charged complexes. Note that in the neutral $[LM—CO]^0$ complexes the C—O bond length is very close to the length of this bond in the free CO molecule for M = Cu and Zn, and for M = Co and Ni the bond is a little longer (see Table 3), which can also be caused by a high contribution of back donation in the Co and Ni complexes.

Table 3 contains the calculated enthalpies of formation (ΔH_f) for complexes **1a—d** and **2a—d** in the neutral, monoanionic, and dianionic forms and for the free CO molecule and its radical anion and dianion. The enthalpies for CO addition to LM^{n-} ($\Delta\Delta H_f$) were calculated from the calculated ΔH_f values

$$LM^{n-} + CO \longrightarrow [LM—CO]^{n-},$$

$$\Delta\Delta H_f = \Delta H_f(LM—CO)^{n-} - \Delta H_f(LM)^{n-} - \Delta H_f(CO)^{n-}$$

$$(n = 0, 1, 2).$$

Assume that the doubly reduced form of the complex (dianion) is the most efficient CO_2-reducing agent, and coordination to the metal of the initial reduction product (CO) is necessary to reduce CO_2 to CH_4. Since the dianionic form of the catalyst is permanently generated on the electrode, it is necessary that CO could be bound to precisely this form. The results of calculations presented in Table 3 show that the enthalpy of CO binding is negative only for the dianionic Cu complex and it is positive for all other complexes studied. This implies that among the studied dianions only $[LCu—CO]^{2-}$ is capable of efficient CO binding and, perhaps, this is a reason for the high yield of CH_4 in electrocatalytic CO_2 reduction involving copper phthalocyanines.

The calculation of the molecular orbitals of the dianions of complexes **2a—d** showed that the HOMO and LUMO of these dianions represent π-orbitals of the ligand, which are not extended to the M—C=O system perpendicular to the ring. The highest of the occupied orbitals and the lowest of the unoccupied orbitals belonging to the M—C=O group for M = Co and Cu are the HOMO-3 (in both cases, the HOMO is occupied by only one electron) and LUMO+1. However, the character of the corresponding orbitals changes sharply on going from Co to Cu.

The fragments of the LUMO+1 and HOMO-3 for the dianions of the Co and Cu complexes are presented in Fig. 3. It is seen that for $[LCo—CO]^{2-}$ the HOMO-3 (calculated energy $\varepsilon = -2.86$ eV) represents a antibonding combination of the d_{xz}-orbital of Co and π*-orbital of CO with a great contribution of the ligand π-orbitals localized mainly on the pyrrole N atoms, and the LUMO+1 ($\varepsilon = 5.78$ eV) is an antibonding combination of the d_{z^2}-orbital of Co and σ*-orbital of CO, also with a contribution from the ligand orbitals. The interaction of the d_{z^2}-orbital with the π*-orbitals is possible because the metal atom is slightly shifted from the ligand plane, and the ligand itself takes the shape of an overturned saucer. Unlike this, for $[LCu—CO]^{2-}$ the HOMO-3 ($\varepsilon = -2.46$ eV) is an antibonding combination of the CO d_{xz}-orbitals and the LUMO+1 ($\varepsilon = 5.86$ eV) is the CO π*-orbital with a minor antibonding contribution from the metal. Among the occupied MOs of $[LCu—CO]^{2-}$,

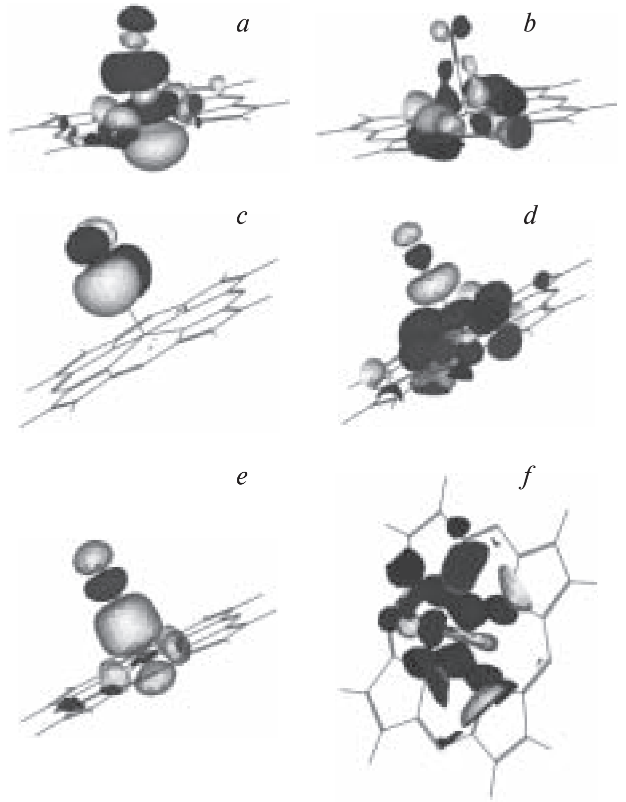


Fig. 3. Fragments of molecular orbitals calculated by the PM3(tm) method: LUMO+1 (*a*) and HOMO-3 (*b*) for $[LCo—CO]^{2-}$, LUMO+1 (*c*) and HOMO-3 (*d*) for $[LCu—CO]^{2-}$, HOMO-41 for $[LCu—CO]^{2-}$ (*e*), and HOMO-30 for $[LCo—CO]^{2-}$ (*f*) (L is the tetraazaporphyrin dianion).

there are two more σ-orbitals, which are antibonding combinations of the Co d_{z^2}-orbital and CO σ*-orbital; these are the HOMO-8 (ε = –3.56 eV) and HOMO-14 orbitals (ε = –5.70 eV) and, finally, the HOMO-41 orbital (ε = –12.23 eV) representing a bonding combination of the Co d_{z^2}-orbital and CO σ*-orbital (see Fig. 3, *e*).

None of the orbitals, which can be treated as an antibonding combination of the Co d_{z^2}-orbital and CO σ*-orbital, was found among the $[LCo—CO]^{2-}$ occupied orbitals. However, the bonding combination of the Co d_{z^2}-orbital and CO σ*-orbital is suitable according to the symmetry for the pair to the orbital presented in Fig. 3, *a*. This is the low-lying HOMO-52 orbital (ε = –18.81 eV). An interesting orbital HOMO-30 is presented in Fig. 3, *f*, in which the CO σ*-orbital interacts with the horizontal orbital *via* the antibonding manner.

Thus, the results of calculation of the molecular orbitals agree with the above arguments favoring the fact that CO coordination to the metal atom of the dianion in the Cu complex occurs by electron occupation of σ-orbitals, whereas Co preferentially binds CO by d—π-interaction.

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