Triphenylphosphane and its derivatives effects on the redox properties of cobalt and copper complexes with Schiff base ligands

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Received 25 November 1982

Accepted for publication 28 June 1983

The redox properties of *N,N'*-ethylenebis(thioacetylacetoniminato)cobalt(II) and *N,N'*-ethylenebis(thioacetylacetoniminato)copper(II) complexes (CoN_2S_2 and CuN_2S_2) were studied by cyclic voltammetry at a platinum electrode in methanol solution.

In the presence of triphenylphosphane, tritolylphosphane, and tris-(3-chlorophenyl)phosphane, which are supposed to enter the coordination sphere of complexes, the redox potential of the electrode reaction $\{CoN_2S_2\}^+ + e^- \rightleftarrows CoN_2S_2$ was shifted to lower values (as a consequence of the preferential coordination of arylphosphane to $\{CoN_2S_2\}^+$). In this case also the effect of a substituent on the benzene ring of arylphosphane was studied. The redox potential of the reaction $\{CuN_2S_2\}^+ + e^- \rightleftarrows CuN_2S_2$ was analogically influenced by the present triphenylphosphane and its derivatives, respectively, however, not to the extent, as for the above complex. In this case no effect of the remote substituent was observed.

Окислительно-восстановительные свойства *N,N'*-этиленбис(тиоацетилацетониминато)кобальтового комплекса (CoN_2S_2) и *N,N'*-этиленбис(тиоацетилацетониминато)медного комплекса (CuN_2S_2) были изучены методом циклической вольтаметрии на платиновом электроде в растворе метанола.

В присутствии трифенилфосфана, тритолилфосфана и трис(3-хлорфенил)фосфана, которые предположительно входят в координационную сферу комплексов, редокс-потенциал электродной реакции $\{CoN_2S_2\}^+ + e^- \rightleftarrows CoN_2S_2$ был сдвинут в сторону более низких значений (вследствие предпочтительной координации арилфосфанов с $\{CoN_2S_2\}^+$). В данном случае изучалось также и влияние заместителя в бензольном кольце арилфосфана. Редокс-потенциал реакции $\{CuN_2S_2\}^+ + e^- \rightleftarrows CuN_2S_2$ аналогичным образом подвергался влиянию присутствующего трифенилфосфана или его производных, однако не так сильно, как вышеописанный кобальтовый комплекс. Кроме того, в этом случае не наблюдалось влияние дальнего заместителя.

The present paper is a further part of the systematic study of redox properties of Co(II) and Cu(II) complexes with *N,N'*-ethylenebis(thioacetylacetonimine) ligand [1, 2], which showed to be suitable model compounds for studying the equatorial-axial interactions and their consequences on the stereochemistry and reactivity of complexes [3]. Its aim was to investigate, to what extent the redox properties of the said complexes would change in the presence of some arylphosphanes, which are able to enter axial positions of the coordination sphere of complexes. The electrochemical study of the mentioned complexes was already dealt with in the literature [4—6], however, with another aim than followed by our work.

Experimental

The complexes of *N,N'*-ethylenebis(thioacetylacetoniminato)cobalt(II) and *N,N'*-ethylenebis(thioacetylacetoniminato)copper(II) were prepared by the method presented in the literature [7]. The cobalt complex (CoN_2S_2) was prepared by the said method directly in an electrolyzed vessel because of its instability toward atmospheric oxygen. Therefore the solvent chosen for experiments was methanol.

Triphenylphosphane (TPP), tritolylphosphane (TTP), and tris(3-chlorophenyl)phosphane (TClPP) were synthesized using processes published in the literature [8].

Commercially available methanol was purified by the standard procedure.

Tetrabutylammonium perchlorate (TBAP) was prepared by the reaction of tetrabutylammonium hydroxide with perchloric acid and then recrystallized from an ethanol—water (volume ratio 4:1) mixture.

Electrochemical measurements were done with a polarograph OH 105 (Radelkis, Budapest) in three-electrode arrangement. For working and auxiliary electrodes platinum wires were used, while an aqueous saturated calomel electrode served as reference electrode. This electrode was separated from the measured solution by a bridge filled with a solution of the solvent and the supporting electrolyte.

All measurements were done in methanol solutions containing 0.05 mol dm^{-3} TBAP as supporting electrolyte. Argon atmosphere was used with a depolarizer concentration in the range of 10^{-4}—10^{-3} mol dm^{-3} at room temperature. Arylphosphane was stepwise added to the system until further addition did not cause any change of the observed redox properties. The ratio of *n*(arylphosphane) : *n*(complex) (*n* is amount of substance) was in the interval of 1—20. The potential scan rate was $v = 66.6$ mV s^{-1}.

Results and discussion

CoN_2S_2

The oxidation of CoN_2S_2 complex in methanol in the presence of one of the above-mentioned arylphosphanes was studied. Fig. 1 shows a typical voltammogram of oxidation of CoN_2S_2 complex with and without the presence of TPP. In all

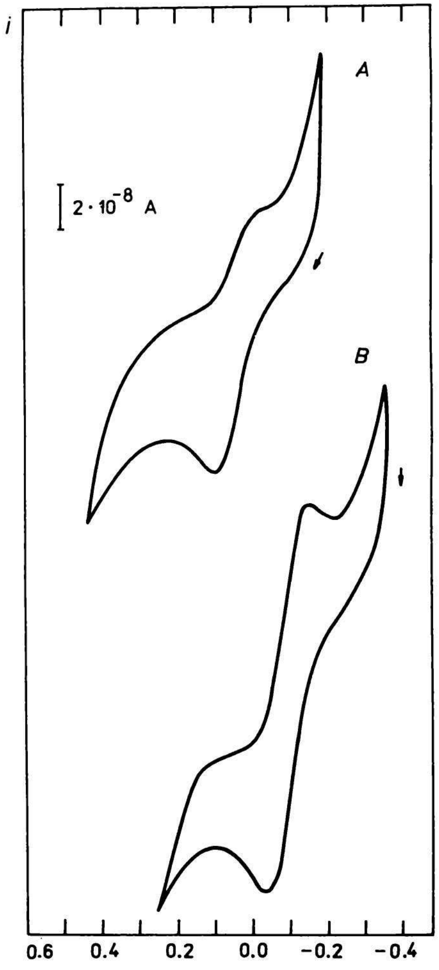

Fig. 1. Cyclic voltammograms of the complex CoN_2S_2 without (*A*) and with (*B*) TPP.

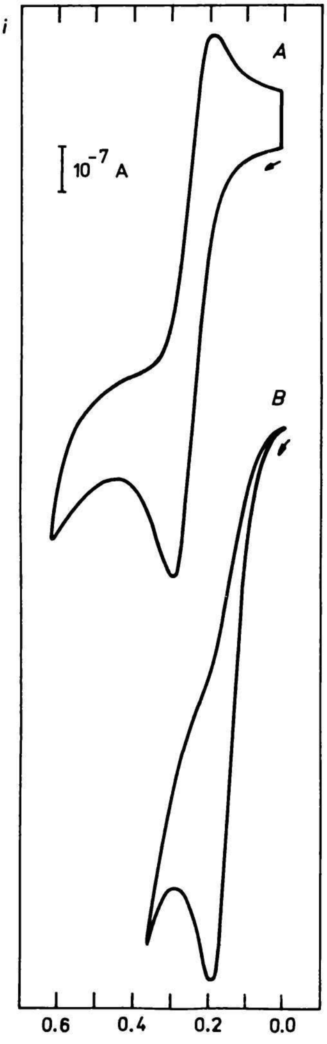

Fig. 2. Cyclic voltammograms of the complex CuN_2S_2 without (*A*) and with (*B*) TPP.

the cases the one-electron oxidation of CoN_2S_2 yielded one oxidation peak and in the direction of the potential reduction one corresponding reduction peak. The separation of the oxidation peak potential $E_{p,a}$ and that of the reduction peak $E_{p,c}$ was in the range of 110—120 mV for the given potential scan rate. From the difference $E_{p,a} - E_{p/2,a} = (77 \pm 7)$ mV the charge transfer coefficient was calculated to be $\alpha = 0.62$ [9]. The presence of one of the arylphosphanes in the system caused a considerable shift of the redox potential $(E'_{1/2} = (E_{p,a} + E_{p,c})\ 2^{-1})$ to lower values (Table 1).

Table 1

Change of the redox properties of CoN_2S_2 complex in the presence of an arylphosphane L

L	$\Delta E'_{1/2}(L)/V^a$	$\Delta\Delta E'_{1/2}/V^b$	σ^c
TPP	−0.18	0.00	—
TTP	−0.20	−0.02	$\sigma_p^+ = -0.31$
TClPP	−0.16	0.02	$\sigma_m = 0.37$

a) $\Delta E'_{1/2}(L) = E'_{1/2}(CoN_2S_2 + L) - E'_{1/2}(CoN_2S_2)$
b) $\Delta\Delta E'_{1/2} = \Delta E'_{1/2}(L) - \Delta E'_{1/2}(TPP)$
c) Ref. [10].

Based on the above presented result it may be stated that arylphosphane preferably undergoes axial coordination to the oxidized form of the complex, *i.e.* that by axial coordination of the arylphosphane the oxidized form becomes more stabilized than the reduced form. The result obtained also confirms the observed ratio between the cathodic and the anodic peak current $i_{p,c}/i_{p,a}$, which at the observation of the oxidation of CoN_2S_2 complex itself exhibits a value in the interval of 0.6—0.7. The presence of one of the arylphosphanes in the system under the same experimental conditions increased this value to equal to one or close to one (TClPP).

The redox behaviour of the complex under investigation is also rather sensitive to the electronic properties of the substituent present on the benzene ring of the triphenylphosphane derivatives. For TTP the CH_3 substituent being in *para* position causes the redox behaviour to decrease by 0.02 V, while the Cl substituent occupying the *meta* position (TClPP) brings about an increase of the redox properties by the same value (of 0.02 V) compared with hydrogen (TPP) (Table 1).

The observed facts are in agreement with the electronic properties of the said substituents. Using the linear energy relationship [10]

$$\Delta E'_{1/2} = \varrho \Sigma \sigma \qquad (1)$$

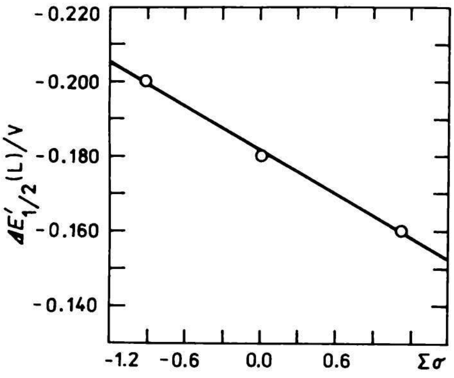

Fig. 3. Redox potentials $\Delta E'_{1/2}(L)$ as a function of the sum of Hammett parameters of the substituent.

where ϱ is the reaction constant and σ the Hammett's substituent parameter, a linear correlation between $\Delta E'_{1/2}$ and $\Sigma\sigma$ was found (Fig. 3) with the reaction constant value of $\varrho = 0.019$ V. Compared with literature data, where the effect of the substituent on the benzene ring was studied [11], this value is lower; this may be assigned to the presence of phosphorus, through which the electronic effects were transferred.

As the results of the presented type show, the redox potential of the $\{CoN_2S_2\}^+$-/CoN_2S_2 system is dependent on the electronic properties of the ligand in axial position and it may also be influenced by electronic effects of the substituents of this ligand.

CuN_2S_2

Under the same conditions as CoN_2S_2 also the CuN_2S_2 complex was studied. A typical voltammogram of one-electron oxidation of the CuN_2S_2 complex with and without TPP presence is shown in Fig. 2. The difference of $E_{p,a} - E_{p/2,a}$ was (70 ± 6) mV, indicating a quasi-reversible electrode reaction [9], the charge transfer coefficient α of which showed the value of 0.69. The ratio $i_{p,c}/i_{p,a}$ was close or equal to one.

The oxidation process of the complex itself was accompanied by an anodic peak and on decreasing the potential by a corresponding reduction peak. In the presence of one of the arylphosphanes in the investigated electrochemical region, the peak belonging to the reduction of the oxidized form disappears, while the anodic peak is shifted to lower potential values (except TClPP) (Table 2).

The disappearance of the reduction peak may be explained by the reduction of the oxidation product by means of the arylphosphane present. Probably also the original CuN_2S_2 complex is to a certain extent product of the reduction, as it is to be

Table 2

Change of the redox properties of CuN_2S_2 complex in the presence of an arylphosphane L

L	$\Delta E_{p,a}(L)/V^a$
TPP	−0.11
TTP	−0.11
TClPP	0.00

a) $\Delta E_{p,a}(L) = E_{p,a}(CuN_2S_2 + L) - E_{p,a}(CuN_2S_2)$

seen on the voltammogram by an increase of the anodic current (except TClPP). Its quantity formed differs, however, according to the circumstance, which of the arylphosphanes is present in the system. This also indicates that the reduction rate is different for each selected arylphosphane. This problem was, however, not studied in the present work and would require a more detailed investigation.

Since the chemical reaction of reduction runs more rapidly than the electrochemical reduction of the oxidation product can be realized, in the presence of one of the arylphosphanes it was not possible to observe the electrochemical reduction of the product of CuN_2S_2 electrooxidation.

In the case of TClPP no coordination to CuN_2S_2 complex takes place, so that no redox changes were seen, but this arylphosphane causes — as also other two do — the missing of the reduction peak on the voltammogram. The observed facts may be assigned to steric reasons (Cl substituent in *meta* position) and simultaneously to a partial distortion of the square-planar complex configuration [12]. No effect of the substituent on the benzene ring of triphenylphosphane (CH_3, Cl) on the redox properties was found for this complex.

Dependence of redox potentials of the studied complexes on the arylphosphanes present reflects the preferential coordination of arylphosphanes to the oxidized form of the complex, *i.e.* the relative stabilization of the oxidized form of the complex compared with the reduced one. These findings are in agreement with the electronic structure of complexes [13], according to which the unpaired electron of CoN_2S_2 appearing in the electrode reaction is prevailingly localized on the cobalt atom out of the complex plane (d_{yz} orbital). For the CuN_2S_2 complex the unpaired electron acting in the electrode process is also localized for the most part on the copper atom, however, in the complex plane (d_{xy} orbital).

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Translated by T. Guttmannová