

Investigation of Gasochromic Rhodium Complexes Regarding Their Reactivity towards CO [†]

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Abstract: The detection of the toxic gas carbon monoxide (CO) in the low ppm range is required in different applications. We present a study of the reactivity of different gasochromic rhodium complexes towards the toxic gas carbon monoxide (CO). Therefore, the binuclear rhodium complexes with different ligands were prepared and their influence regarding reaction velocity and sensitivity towards CO was investigated. The most promising rhodium complex was embedded into a polymer with which glass substrates were coated. The reactivity towards CO of these layers was also investigated.

Keywords: gasochromic; carbon monoxide; gas sensor; rhodium complex

1. Introduction

The detection of the toxic gas carbon monoxide (CO) is especially of high relevance in early fire gas detection, but is also constantly monitored in any industrial or private types of furnaces [1,2]. The required concentration range is in the low ppm range. Several methods of detecting CO are known like electrochemical sensing, metal oxide sensors, or IR spectroscopy. Regarding the aim of sensors to become as small as possible, energy-efficient, and low-cost, the approach of detecting gases via gasochromic dyes came to the fore during the last few years. However, first gasochromic determination of CO using iodine pentoxide (I₂O₅) was described in 1929 [3]. Another suitable inorganic compound is based on a silico-molybdate complex with palladium chloride as catalyst [4]. However, the reaction of inorganic compounds with CO is only reversible in some cases and usually under high energy supply. Better reversibility is given by metal complex dyes like 5,10,15,20-tetraphenylporphyrin iron(III) chloride or 5,10,15,20-tetraphenylporphyrin zinc(II) [5,6]. Binuclear rhodium complexes showed a fast and selective reaction towards CO [7–10]. Furthermore, these compounds offer the advantage of a reversible CO reaction. Therefore, we prepared several binuclear rhodium complexes starting from the dimer rhodium(II) acetate. For evaluation of the reaction velocity towards CO, the color change while applying CO was recorded of both the dissolved rhodium complexes as well as the compounds embedded into a polymer. These results show the opportunity of using rhodium complexes prepared as gas-sensitive layers on glass substrates for the selective and reversible detection of CO in air.

2. Experimental Part

2.1. Synthesis of Binuclear Rhodium Complexes

As indicator for CO binuclear rhodium complex with different ligands were synthesized according to a procedure described in literature [8]. By varying the residues of the phosphines three different compounds based on the identical basic structure were obtained (see Figure 1 and Table 1).

Table 1. Ligands of the rhodium compounds **1·(A)₂**–**3·(A)₂**.

Compound	X=	R=	A=
1·(A)₂	p-OCH ₃	CH ₃	CH ₃ CO ₂ H
2·(A)₂	m-CH ₃	CH ₃	CH ₃ CO ₂ H
3·(A)₂	m-F	CH ₃	CH ₃ CO ₂ H

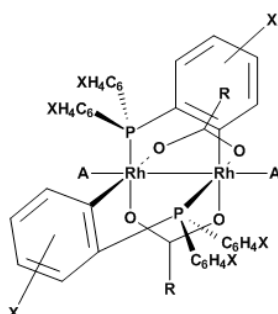


Figure 1. Chemical structure of the colorimetric binuclear rhodium complex $\text{Rh}_2(\text{O}_2\text{CCH}_3)_2(\text{P}(\text{C}_6\text{H}_4\text{X})_2)_2 \cdot \text{A}_2$ with different ligands (see Table 1).

0.45 mmol (200 mg) rhodium acetate dimer were dissolved in a mixture of 25 mL toluene and 5 mL acetic acid and 0.90 mmol of the corresponding phosphine were added. After refluxing the mixture at 125 °C for 3 h the purple solution was cooled to ambient temperature. The solvent was removed under reduced pressure at ambient temperature to yield a deep purple powder.

The rhodium complexes were characterized by FTIR spectroscopy (Bruker ALPHA-T) and differential scanning calorimetry (Netzsch DSC 204 F1; heat rate 10 K/min¹).

1·(A)₂ Yield: 87%. FTIR (KBr, cm^{−1}): 3432 (w), 3064 (vw), 2995 (w), 2935 (m), 2903 (w), 2834 (m), 2618 (vw), 2543 (w), 2050 (w), 1893 (w), 1678 (s), 1592 (vs), 1566 (vs), 1502 (vs), 1485 (s), 1429 (s), 1404 (s), 1366 (m), 1342 (m), 1287 (vs), 1249 (vs), 1218 (s), 1179 (vs), 1121 (m), 1096 (s), 1028 (s), 941 (w), 862 (w), 825 (s), 796 (s), 717 (w), 689 (m), 619 (m), 598 (w), 547 (s), 501 (m), 466 (m), 432 (m). DSC: 149 °C (dec.).

2·(A)₂ Yield: 92%. FTIR (KBr, cm^{−1}): 3432 (w), 3050 (vw), 3009 (w), 2918 (m), 2862 (w), 2618 (vw), 2548 (w), 2355 (vw), 1678 (vs), 1569 (s), 1474 (m), 1446 (s), 1410 (s), 1367 (m), 1335 (m), 1294 (s), 1243 (m), 1219 (vw), 1172 (w), 1138 (w), 1107 (m), 1083 (w), 1024 (m), 994 (vw), 940 (vw), 869 (w), 815 (m), 777 (m), 724 (w), 693 (s), 631 (vw), 612 (vw), 558 (m), 530 (w), 469 (s), 431 (vw). DSC: 214 °C (dec.).

3·(A)₂ Yield: 97%. FTIR (KBr, cm^{−1}): 3432 (w, b), 3064 (w), 2927 (w, b), 2678 (vw), 2620 (w, b), 2554 (w, b), 2358 (vw), 1671 (vs), 1600 (m), 1576 (vs), 1475 (s), 1417 (vs), 1364 (m), 1342 (m), 1295 (m), 1262 (m), 1244 (s), 1217 (vs), 1186 (m), 1164 (w), 1138 (vw), 1117 (w), 1096 (m), 1067 (w), 1046 (vw), 1024 (m), 997 (w), 893 (m), 876 (m), 820 (w), 783 (m), 720 (w), 687 (vs), 631 (vw), 614 (w), 591 (m), 573 (m), 523 (m), 493 (s), 453 (w), 414 (w). DSC: 231 °C (dec.).

2.2. Fabrication of the Gas-Sensitive Layers

For the sensitive layers, the rhodium complex (**1·(A)₂**, **2·(A)₂**, or **3·(A)₂**) was dissolved in toluene or chloroform (CHCl₃) and mixed with a solution containing the matrix ethyl cellulose (EC) and the plasticizer tributyl phosphate (TBP). In Table 2 the composition of the solution for the preparation of the sensitive layers is given.

Table 2. Composition of the solution with the colorimetric compounds.

Solution #	Composition
S1	5 mg 1·(A) ₂ in 1 mL CHCl ₃ + 5 mL matrix solution (750 mg EC, 750 mL TBP, 30 mL ethanol)
S2	6 mg 2·(A) ₂ in 1 mL toluene + 3 mL matrix solution (750 mg EC, 750 mL TBP, 30 mL toluene)
S3	6 mg 3·(A) ₂ in 1 mL toluene + 3 mL matrix solution (750 mg EC, 750 mL TBP, 30 mL toluene)
S4	12 mg 1·(A) ₂ + 1 mL matrix solution (750 mg EC, 750 mL TBP, 30 mL toluene)
S5	11 mg 2·(A) ₂ + 1 mL matrix solution (750 mg EC, 750 mL TBP, 30 mL toluene)
S6	11 mg 3·(A) ₂ + 1 mL matrix solution (750 mg EC, 750 mL TBP, 30 mL toluene)

Each solution was pipetted onto glass substrate to investigate the drying behavior regarding homogeneity, transparency, and adhesion. By varying the solution amount and repeating the process, different thicknesses between 5 µm and 40 µm could be obtained.

2.3. Gas Sensing Experiments

To investigate the spectral response of the deposited colorimetric layers, the solution was pipetted onto a glass window of a gas-tight cell for measurements in an UV-VIS spectrometer (Lambda900, Perkin Elmer). The solution was dried for 24 h and exposed to 200 ppm CO for 60 min at a gas flow of 1 L/min. For all measurements shown are relative humidity of 40% was given.

3. Results and Discussion

Upon CO exposure, the rhodium complexes change their colour from purple through red and orange to yellow. The spectral response from 250 nm to 850 nm of 11 mg **1·(A)**₂ dissolved in 8 mL chloroform before and after exposure to CO (200 ppm, 8 min) is depicted in Figure 2.

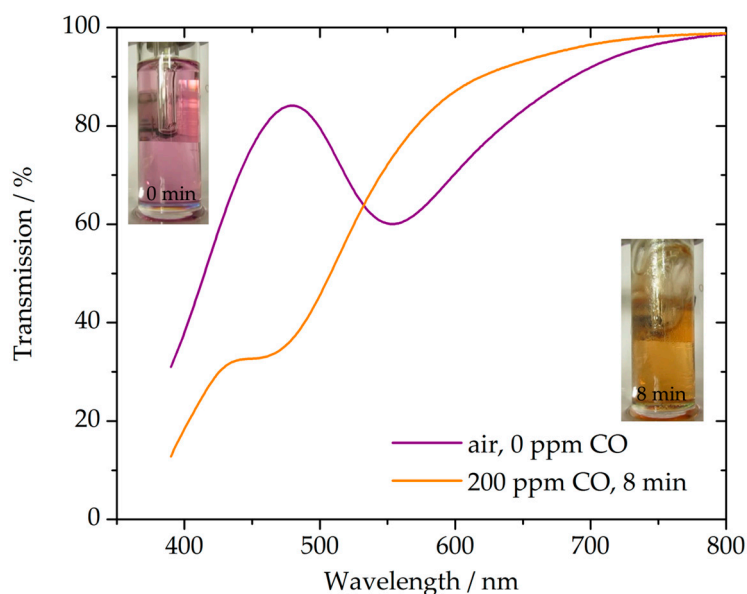


Figure 2. Spectral response of rhodium complex **1·(A)**₂ (11 mg dissolved in 8 mL CHCl₃) before (purple) and after exposure to CO (yellow) [10].

The colour change of the prepared rhodium complexes is caused by a reversible two-step ligand exchange depicted in Figure 3.

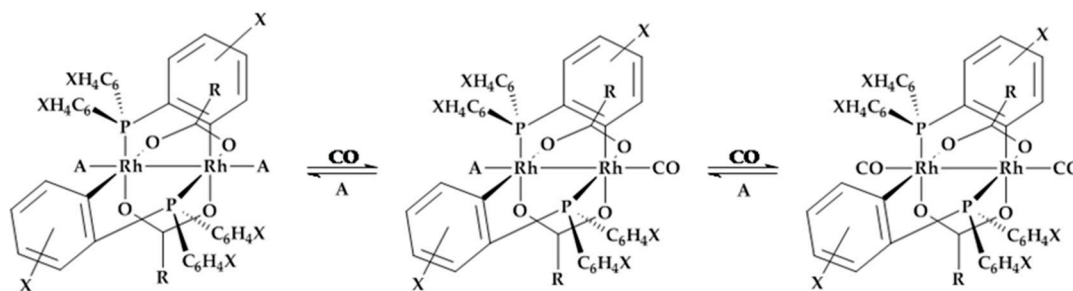


Figure 3. Reaction scheme of the rhodium complex with CO.

All rhodium complexes $1\cdot(A)_2$ – $3\cdot(A)_2$ were dissolved in toluene (10 mmol in 15 mL) and exposed to 200 ppm CO for 10 min. Thereby, all solutions turned from purple through orange to yellow. Thereby, compound $2\cdot(A)_2$ showed the fastest and compound $3\cdot(A)_2$ the slowest reactivity with CO. This can be explained by the more or less electron donating residues X of the phosphine ligands. In all cases a much slower reverse reaction was observed after stopping CO exposure.

Furthermore, the prepared layers from solutions S1–S6 onto UV/VIS glasses were characterized via UV/VIS spectroscopy. As expected, the reaction of embedded rhodium complexes with CO is much slower than in solution even at higher CO concentrations (Figure 4).

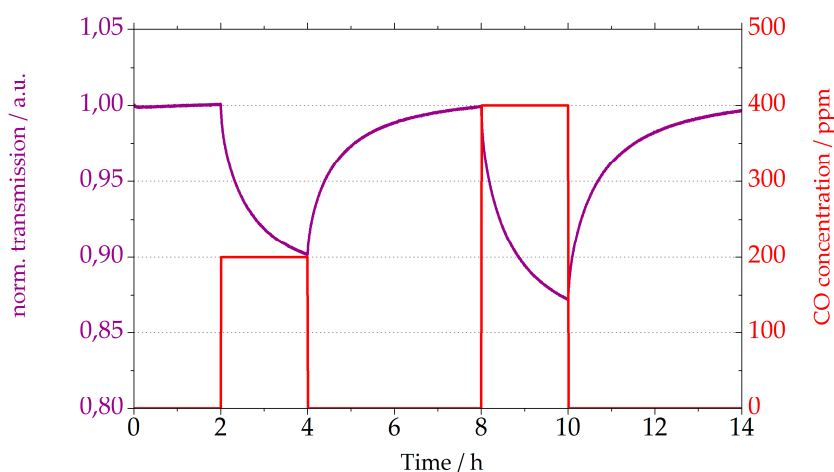


Figure 4. Normalized transmission change at 420 nm of $1\cdot(A)_2$ in EC (S1) at 200 and 400 ppm CO [10].

4. Conclusions

Three gasochromic binuclear rhodium complexes were prepared and characterized. Their reaction velocity towards CO was recorded of both the dissolved compounds as well as embedded into a polymer. These results show the opportunity of using rhodium complexes prepared as gas-sensitive layers on glass substrates for the selective and reversible detection of CO in air.

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Conflicts of Interest: The authors declare no conflict of interest.

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