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Progress in the Chromogenic Detection of Carbon Monoxide**

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Carbon monoxide gas is referred to as "silent killer" because of its high toxicity and the inability of humans to detect it without using appropriate technology. CO detectors can be installed indoors and warn people about a dangerous CO concentration and thus protect them from this highly toxic inhalant. Carbon monoxide concentrations of 400 ppm are lethal within minutes, and the maximum CO exposure for adults is limited to 50 ppm over an eight hour period.

Carbon monoxide sensing can be based either on semiconductor, electrochemical, chemical, or biomimetic principles. CO detectors are most often based on semiconducting metal oxides.[1] Upon exposure to molecular oxygen, negatively charged oxygen species (O_2^- or O^-) accumulate on the surface of, for example, SnO_2, TiO_2, or ZnO crystals, with formation of less conductive zones. CO gas, which can act as a reductant, reacts with the surface oxygen species to from CO_2. As a consequence, the electrical conductance of the metal oxide film increases, thus triggering a response of the sensor.

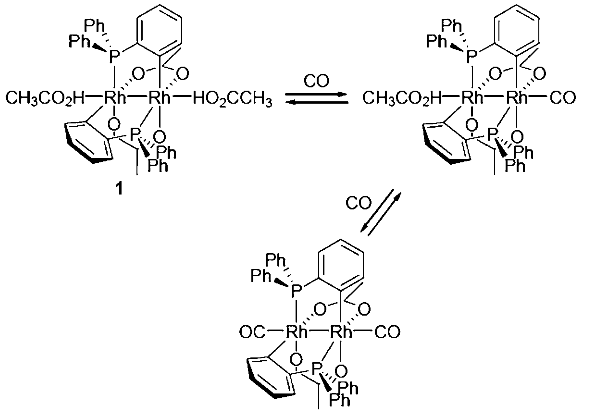
Semiconducting metal oxide sensors can be compounds that are pure or doped with different kinds of metals. Sensors based on constant potential amperometry (that is, current measurement when applying constant external voltage) and catalytic combustion are commercially available for the detection of CO.[2] Both types of sensors exploit the oxidation of carbon monoxide as a sensing principle. The first type operates by measuring the electrolytic current caused by oxidation of CO into CO_2, while the second type measures the change of resistance in a Pt wire, where the change is caused by the heat released upon catalytic CO oxidation.

Optochemical detectors containing a sensitive chemical compound that changes its optical properties upon reaction with the toxic molecule can be more simple and potentially cheaper than metal oxide sensors. The shortcomings of visual warning but especially the lack of sensitivity and selectivity of existing colorimetric probes in the critical concentration range presently reduce the quality of protection against CO poisoning.

Iron, ruthenium, and rhodium complexes have been investigated as colorimetric CO sensors.[3–6] Synthetic iron compounds are sensitive to CO and mimic its action on human hemoglobin.[6] However, the color change is often rather limited and spectroscopic techniques have to be used in order to detect the signal. Disadvantages of previously reported optochemical systems are the rather high detection threshold, the lack of CO sensing capacity in ambient air, and potential interference of other airborne chemical compounds.

Recently, significant progress has been made in chemical CO sensor development. Gulino et al.[3] developed a glass-supported dirhodium complex that is highly selective for CO and has a detection limit at the ppm level. However, this complex shows only modest color changes in the visible region, thus UV/Vis spectroscopy must be used as a detection tool.

In a recent Communication in this journal, Esteban et al.[7] reported a binuclear rhodium complex **1** (Scheme 1) as a chromogenic system for CO sensing. The unique chemical properties of complex **1** apparently overcome previous shortcomings of molecules for CO sensing. The electron density of the metals was modulated with phosphine ligands in a head-to-tail arrangement to facilitate electron back-donation from Rh orbitals to the π* molecular orbital of CO. Ligand



Scheme 1. Dirhodium complex **1**, which was identified as a highly sensitive and reliable CO probe that functions by axial ligand exchange.[7]

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exchange in axial positions on binuclear rhodium complexes are known to cause intense color changes.[8] The research group of Martínez-Máñez previously investigated the use of other chromogenic systems for the determination of methylmercury[9] and anionic surfactants in surface water,[10] and is now successful in area of CO sensing.

The dirhodium complex **1** is capable of CO sensing both in solution and in air, and therefore offers an important advantage compared to earlier reported complexes. The color change of the complex from violet to orange is readily observable by the naked eye and occurs within minutes at the critical CO concentration of 50 ppm (Figure 1). The detection limit can be as low as 0.5 ppm when a spectrometer is used. The absorption intensity increases linearly in the critical CO concentration range of 0–100 ppm. The visual detection of CO at the critical concentration certainly is an advantage compared to earlier available chemical probes.

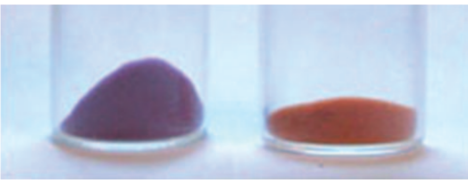

Figure 1. Color change of silica gel supported **1** upon CO ligand exchange in the presence of air containing 50 ppm CO (picture courtesy of the authors).[7]

The CO probe **1** can conveniently be regenerated in a stream of air under ambient conditions. The very high specificity for CO is also noteworthy. The complex is inert toward a variety of atmospheric compounds including CO_2, N_2, O_2, Ar, CH_4, SO_2, NO_x, and volatile organic compounds. Only very high NO_x concentrations, which do not occur under normal conditions, can interfere by ligand exchange and subsequent color change.

The dirhodium complex discovered by Esteban et al. is a reversible highly selective colorimetric sensor for carbon monoxide. An attractive feature is the very clear induced color change, which enables the detection of toxic CO concentrations by the naked eye. According to the authors,[11] adequate Rh complex/silica carrier weight ratios are from 1:10 to 1:1. The photograph in Figure 1 shows a solid that has a Rh complex/silica weight ratio of 1:3.[11] A reduction of the quantity of precious metal complex needed for chromogenic CO sensing remains a challenge for further research.

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[1] P. K. Dutta, R. R. Rao, S. L. Swartz, C. T. Holt, *Sens. Actuators B* **2002**, *84*, 189–193.

[2] N. Izu, S. Nishizaki, T. Itoh, M. Nishibori, W. Shin, I. Matsubara, *Sens. Actuators B* **2009**, *136*, 364–270.

[3] A. Gulino, T. Gupta, M. Altman, S. Lo Schiavo, P. G. Mineo, I. L. Fragalà, G. Evmenenko, P. Dutta, M. E. Van der Boom, *Chem. Commun.* **2008**, 2900–2902.

[4] S. Paul, F. Amalraj, S. Radhakrishnana, *Synt. Math.* **2009**, *159*, 1019–1023.

[5] J. M. Barbe, G. Canard, S. Brandès, R. Guilard, *Chem. Eur. J.* **2007**, *13*, 2118–2129.

[6] D. Benito-Garagorri, M. Puchberger, K. Mereiter, K. Kirchner, *Angew. Chem.* **2008**, *120*, 9282–9285; *Angew. Chem. Int. Ed.* **2008**, *47*, 9142–9145.

[7] J. Esteban, J. V. Ros-Lis, R. Martínez-Máñez, M. Dolores Marcos, J. Soto, F. Sancenón, *Angew. Chem.* **2010**, *122*, 5054–5057; *Angew. Chem. Int. Ed.* **2010**, *49*, 4934–4937.

[8] P. Hirva, J. Esteban, P. Lahuerta, J. Pérez-Prieto, *Inorg. Chem.* **2007**, *46*, 2619–2626.

[9] E. Climent, M. Dolores Marcos, R. Martínez-Máñez, F. Sancenón, J. Soto, K. Rurack, P. Amorós, *Angew. Chem.* **2009**, *121*, 8671–8674; *Angew. Chem. Int. Ed.* **2009**, *48*, 8519–8522.

[10] C. Coll, R. Martínez-Máñez, M. Dolores Marcos, F. Sancenón, J. Soto, *Angew. Chem.* **2007**, *119*, 1705–1708; *Angew. Chem. Int. Ed.* **2007**, *46*, 1675–1678.

[11] R. Martínez-Máñez, personal communication.