Investigation of Imidazol(in)ium-dithiocarboxylates as Sensors for the Detection of Mercury(II) and Silver(I) Ions

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Two imidazol(in)ium-dithiocarboxylates have been investigated as sensors for the detection of mercury ions and silver ions. They could be applied as colorimetric chemosensors for the detection of Hg\(^{2+}\) and Ag\(^{+}\). Furthermore, an additional sensory input was found by a colorimetric change of a two-phase system from the organic phase into the aqueous phase. Due to different colors at different ratios of the betaines and Hg\(^{2+}\) it is possible to estimate the concentration of Hg\(^{2+}\) with the "naked eye".

Key words: Carbenes, Imidazolium-dithiocarboxylates, Mercury, UV/Vis, Betaines

Introduction

Imidazol(in)ium-dithiocarboxylate betaines, formal adducts of carbenes and CS\(_2\) are composed of a positively charged imidazolium ring and a negatively charged CS\(_2\) group tilted almost perpendicular to the ring [1 – 4]. These betaines were first reported by Winberg and Coffman in 1965 [5]. Thereafter, their chemistry, like their application in [3 + 2] cycloaddition reactions with electron-deficient alkynes, was studied by several groups [6 – 22]. The compounds are known to be stable [1 – 4] contrary to their CO\(_2\) and COS analogs [1, 4]. In addition, the synthesis of several metal complexes with these betaines as ligands have been reported [23 – 32], and recently a few investigations of reactions catalyzed by metal complexes of these betaines have been described [33 – 35]. Moreover, the group of Delaude found that these compounds could be used for probing the stereoelectronic parameters of N-heterocyclic carbenes [36].

Recently, we reported the application of symmetric imidazolinium-dithiocarboxylates as organocatalysts for the TMSCN addition on aldehydes [37] and of enantiopure analogs as organocatalysts for an asymmetric Staudinger reaction [38]. In addition, we prepared new ionic liquids via methylation of the corresponding betaines, resulting in red cations, which showed different absorptions maxima depending on the solvent and the lipophilicity of the anions [39]. In order to further investigate the behavior of these betaines, we present here the evaluation of this class of compounds as sensors for different metal ions. Hg\(^{2+}\) ions for example possess a high affinity to sulfur, thus these betaines offer the possibility to serve as ligands for binding with Hg\(^{2+}\) due to the CS\(_2\) group [32]. Furthermore, a visual color change can be expected, since the binding of Hg\(^{2+}\) to CS\(_2\) would change the electron density of the CS\(_2\) unit and hence change the charge-transfer system between the CS\(_2\) group and the imidazol(in)ium ring.

Mercury is a highly toxic element, accumulating readily as inorganic mercury compound in the environmental water, where it can be converted into the even more toxic methylated mercury, which may enter the food chain by eating contaminated fish [40, 41]. A simple and straight forward method to detect mercury contaminations, without the need of a large experimental setup and instrumentation, is the application of colorimetric chemosensors [42 – 44]. Several types of chemosensors for Hg\(^{2+}\) have been developed, and their number has increased continuously [45 – 53]. A larger number of examples of these chemosensors are based on ferrocenes [54, 55], rhodamines [56 – 58], naphthalimides [59, 60],
4,4-difluoro-4-bora-3a,4a-diaza-s-indacenes [61, 62], anthracenes [63, 64], porphyrins [65, 66], and β-cyclodextrins [67, 68].

Here we present the investigation of a new simple straightforward motif for a sensor for mercury(II) and silver(I) cations.

Results and Discussion

Two different betaines were prepared according to Scheme 1. Starting from the literature-known imidazolinium salt 1 or the commercially available imidazolium salt 2, the corresponding carbenes were prepared with KOrBu as the base. The in-situ prepared carbenes were reacted with CS2 to the desired betaines 3 and 4.

Ideally, a chemosensor for Hg\(^{2+}\) should be applied in an aqueous system. Because the prepared betaine 4 was not or only slightly soluble in water, the first experiments were carried out in methanol. One equivalent of Hg(NO\(_3\))\(_2\) was added to a methanol solution of each betaine. Compound 4 generated the most significant color change from red to purple (Fig. 1). This appears plausible, since the π-electron system in 4 is more delocalized.

The selectivity towards Hg\(^{2+}\) was tested by measuring UV/Vis absorption spectra for other metal nitrates namely Zn(NO\(_3\))\(_2\), Co(NO\(_3\))\(_2\) and Cd(NO\(_3\))\(_2\). These spectra and the color changes are illustrated in Fig. 1, which verify that only Hg\(^{2+}\) forms a strong mercury complex by the decrease and the shift of the absorption maximum at about 350 nm toward shorter wavelengths. In addition, a marginal increase and shift toward longer wavelengths of the absorption maximum in the visible range at about 540 nm was observed. The other metal ions did not promote significant changes in the UV/Vis spectra. In order to confirm the formation of a complex between 4 and Hg\(^{2+}\), \(^1\)H NMR and \(^{13}\)C NMR spectra were measured in CD\(_3\)OD before and after the addition of Hg(NO\(_3\))\(_2\) as illustrated in Figs. 2 and 3. The comparison of the spectra shows peak shifts caused by the formed metal complex. The \(^{13}\)C spectrum also provides the information how Hg\(^{2+}\) binds to 4. After adding mercury, the signal of the CS\(_2\) group in the \(^{13}\)C NMR spectrum shifted upfield from 226 to 216 ppm, which corroborates the presumption that the binding of 4 to Hg\(^{2+}\) ion takes places \textit{via} the CS\(_2\) group.

\[ \text{Scheme 1. Synthesis of carbene CS}_2 \text{ adducts.} \]

\[ \text{Fig. 1 (color online). UV/Vis spectra of 4 without and in the presence of various metal ions (1 equiv.) in MeOH. The concentration of the measured solution was 10}^{-5} \text{ mol L}^{-1}. \text{ The photograph of color changes of 4 in MeOH solution (10}^{-2} \text{ mol L}^{-1}) \text{ with 1 equiv. of different metal ions. A: --; B: Zn}^{2+}; C: Co}^{2+}; D: Cd}^{2+}; E: Hg}^{2+}. \]
For clarifying how many equivalents of Hg$^{2+}$ ions impact the color change, 4 was treated with 2 and 4 equiv. of Hg$^{2+}$. While the doubling of equivalents leads to an intensity decrease of the absorption band at about 350 nm and an increase at about 540 nm in the visible range, the quadrupling affects the absorption only marginally. A significant visual color change was not observed.

Because 3 was not soluble in methanol, acetonitrile was used as solvent, to which 1 equiv. of various metal nitrates was added. Similar to 4, only Hg$^{2+}$ caused a significant color change from yellow to pink. This has also been confirmed by the UV/Vis spectra shown in Fig. 4. The addition of Zn$^{2+}$, Co$^{2+}$ and Cd$^{2+}$ did not result in a significant change in the UV/Vis spectra.

Next, the colorimetric behavior of 3 was investigated in a two-phase mixture of water and CHCl$_3$. As shown in the inset of Fig. 5, compound 3 shows a yellow color in the chloroform phase with an absorption maximum centered at about 360 nm and in the visible range at about 430 and 500 nm. After adding an equimolar amount of aqueous Hg(NO$_3$)$_2$ solution and shaking the mixture, the intensity of the absorption band in the near UV range decreased, and the absorption maximum slightly shifted to a longer wavelength. The change in the UV/Vis spectra can also be seen visually by the color change from yellow to pink, obviously caused by the interaction of Hg$^{2+}$ and 3 to a complex at the phase boundary, which remains in the organic phase.

Compound 4 was also investigated with regard to the detection of Hg$^{2+}$ in an H$_2$O-CHCl$_3$ solution. The photography in Fig. 6 shows the two-phase mixture of 4 with and without Hg$^{2+}$. In the latter case the organic
phase shows a red color, while the aqueous phase is colorless to light yellow. The slight coloration to yellow is probably due to a minor solubility of 4 in water or to a small amount of CHCl₃ in the aqueous phase. This is only temporarily, and the color disappears after a few hours. Surprisingly, the addition of Hg²⁺ caused a color change to colorless in the organic phase and to pink in the aqueous phase. Thus, 4 forms a complex with Hg²⁺ at the phase border, which remains in the aqueous phase. The corresponding UV/Vis spectra are shown in Fig. 6, which shows that the absorption band of the organic phase disappears after adding water enriched with Hg²⁺. In contrast, the absorption band of the aqueous phase increases and shifts to shorter wavelengths in the near UV range, and a new absorption band appears at about 550 nm.

To determine the visible detection limit, two samples of 4 were prepared in H₂O-CHCl₃ with a concentration of 10⁻³ mol L⁻¹. One sample was enriched with 1 equiv. of Hg²⁺, shown in Fig. 7. A resulting color change was observed in both phases, however it was very pale. While the organic phases differ only slightly from each other, the aqueous phase of contaminated water can be distinguished from pure H₂O by the color change to light pink. Because a concentration of 4 of 10⁻³ mol L⁻¹ was too low for a significant color change, further investigations were carried out with 4 in the concentration of 10⁻² mol L⁻¹ in CHCl₃-H₂O. The photograph in Fig. 8 shows the resulting two-phase mixtures, which were enriched in the following sequence with 0.1, 0.2, 0.3, 0.4 and 0.5 equiv. of Hg²⁺. For comparison, the
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Fig. 4 (color online). UV/Vis spectra of 3 (10$^{-5}$ mol L$^{-1}$) without and in the presence of different metal ions. The photograph of color changes of 3 in acetonitrile solution (10$^{-2}$ mol L$^{-1}$) by addition of 1 equiv. of different metal ions. F: –; G: Zn$^{2+}$; H: Co$^{2+}$; I: Cd$^{2+}$; J: Hg$^{2+}$.

Fig. 5 (color online). UV/Vis spectra of 3 (10$^{-5}$ mol L$^{-1}$) in a two-phase mixture of H$_2$O and CHCl$_3$ without and with Hg$^{2+}$ (1 equiv.). Photograph of color changes of 3 (10$^{-2}$ mol L$^{-1}$). M: –; N: Hg$^{2+}$.

Fig. 6 (color online). UV/Vis spectra of 4 (10$^{-5}$ mol L$^{-1}$) in a two phase mixture of H$_2$O and CHCl$_3$ without and with Hg$^{2+}$ (1 equiv.). Photograph of color changes of 4 (10$^{-2}$ mol L$^{-1}$). K: –; L: Hg$^{2+}$.

Fig. 7 (color online). Photograph of color changes of 4 (10$^{-3}$ mol L$^{-1}$) in H$_2$O and CHCl$_3$ before (O) and after the addition of 1 equiv. Hg$^{2+}$ (P). Sample without Hg$^{2+}$ is also shown. With the increasing addition of Hg$^{2+}$, the organic phase becomes red to colorless, while the aqueous phase turns from yellow via red to pink. Moreover, it is demonstrated that half of Hg$^{2+}$ to 4 shows the same color change as such, when using the same ratio. The full discoloring of the organic phase suggests that one Hg$^{2+}$ ion is binding to two molecules of 4. The corresponding UV/Vis spectra correspond to the visual color changes. With
Fig. 8 (color online). Photograph of color changes of 4 \((10^{-2} \text{ mol L}^{-1})\) by addition of different amounts of \(\text{Hg}^{2+}\).

- K: –; Q: 0.1 equiv.; R: 0.2 equiv.; S: 0.3 equiv.; T: 0.4 equiv.; U: 0.5 equiv. \(\text{Hg}^{2+}\).

Fig. 9 (color online). UV/Vis spectra of the aqueous phase (A) of 4 \((10^{-2} \text{ mol L}^{-1})\) in a mixture of \(\text{H}_2\text{O}\) and \(\text{CHCl}_3\) with different amounts of \(\text{Hg}^{2+}\).

Increasing \(\text{Hg}^{2+}\) concentration, the absorption bands appear in the case of the aqueous phase and disappear in the organic phase (see Figs. 9 and 10).

The validity of the Lambert-Beer Law was examined by plotting the absorption against different concentrations for a selected wavelength (see Supporting Information available online; see note at the end of the paper for availability). The linearity of the graph showed that only one Hg dye complex is involved in the color change.

The selectivity towards \(\text{Hg}^{2+}\) was investigated by the addition of various metal nitrates (\(\text{Co}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Cu}^{2+}, \text{Ag}^{+}\) and \(\text{Pb}^{2+}\)) dissolved in \(\text{H}_2\text{O}\) to a solution of 4 in \(\text{CHCl}_3\). Since \(\text{Cu}^{2+}, \text{Ag}^{+}\) and \(\text{Pb}^{2+}\) have a similar chemical behavior as \(\text{Hg}^{2+}\), it is difficult to develop sensors reacting selectively with \(\text{Hg}^{2+}\) ions [69–72]. Silver complexes with ligands incorporating a \(\text{CS}_2\) moiety have been reported in the literature [73, 74]. From Fig. 11 it can be seen that only the addition of \(\text{Ag}^{+}\) and \(\text{Hg}^{2+}\) causes a significant color change in both phases. The presence of \(\text{Ag}^{+}\) causes an immediate color change from colorless to deep red in the aqueous phase, also confirmed by UV/Vis spectra in Fig. 11. While the absorption maxima of the organic phase centered at about 360 nm and in the visible range at about 540 nm disappear, the absorption of the aqueous phase increases, resulting in a broad absorption band with a shoulder in the visible range between 500 and 600 nm. Even though \(\text{Ag}^{+}\) provides a color change with 4, it can be distinguished from \(\text{Hg}^{2+}\).

Conclusion

It has been shown that the imidazolium-dithiocarboxylate 4 shows the potential as a chemo-sensor for \(\text{Hg}^{2+}\) and \(\text{Ag}^{+}\). The betaine has not been investigated before for this application. The observed phase change with betaine 4 with silver and mercury complexes may lead to new sensors based on these betaines which are capable to detect two different metal species simultaneously, either remain in the organic phase or transfer into the aqueous phase. In addition, due to the different colors at different ratios of the betaine and \(\text{Hg}^{2+}\), it is possible to estimate the concentration of \(\text{Hg}^{2+}\) with the “naked eye”. Considering the low sensitivity and selectivity of
room temperature. The reactions were followed by thin layer chromatography on silica gel precoated plates (Merck TLC silica gel F254). Column chromatography was performed using silica gel 60. Salt 2 and N,N'-dibenzylenediamine were purchased from Aldrich.

1,3-Dibenzyldimazolium tetrafluoroborate (1)

N,N'-Dibenzyldimazolium tetrafluoroborate (0.74 mL, 3.16 mmol, 1 eq.), triethyl orthoformate (0.53 mmol, 3.16 mmol, 1 eq.) and ammonium tetrafluoroborate (331 mg, 3.16 mmol, 1 eq.) were heated for 2 h at 120 °C in a closed vessel. Recrystallization in dry ethanol gave a colorless solid (953 mg, 2.8 mmol, 89%). M. p. 84 °C. – IR (KBr): ν = 3092, 1649, 1457, 1443, 1373, 1304, 1208, 1058, 704 cm⁻¹. – 1H NMR (200 MHz, CDCl₃): δ = 8.54 (s, 1 H, NCHN), 7.34 (m, 10 H, H-Ar), 4.67 (s, 4 H, NCH₂Ar), 3.74 ppm (s, 4 H, 2 NCH₂CH₂). – 13C NMR (50 MHz, CDCl₃): δ = 157.7 (NCHN), 132.5, 129.4, 129.2, 129.0, 52.4, 47.8 ppm. – MS (ESI, 0 V): m/z (%): 251 (100) [M]+. – Anal. for C₁₇H₁₀N₂BF₄: calcd. C 60.38, H 5.66, N 8.28; found C 59.93, H 5.69, N 8.37.

1,3-Dibenzyldimazolium-2-dithiocarboxylate (3)

1,3-Dibenzyldimazolium tetrafluoroborate (1) (3.16 mmol, 1 eq.) was dissolved in THF (2 mL), and KOrBu (531 mg, 4.74 mmol, 1.5 eq.) was added. After stirring for 30 min CS₃ (0.95 mL, 15.8 mmol, 5 eq.) was added. The mixture became reddish. Water and CH₂Cl₂ were added, and the aqueous layer was extracted 3 times with CH₂Cl₂. The organic layers were dried (Na₂SO₄), and the solvent was removed by evaporation. The obtained product was isolated by column chromatography with CH₂Cl₂ to give a red solid (653 mg, 2 mmol, 63%). Spectral data were consistent with literature values [7]. 13C NMR data are not provided in the literature and are given here. – 13C NMR (100 MHz, CDCl₃): δ = 224.9 (CS₂), 167.0, 133.0, 129.2, 129.1, 129.0, 51.2, 46.0 ppm.

3-Butyl-1-methylimidazolium-2-dithiocarboxylate (4)

3-Butyl-1-methylimidazolium chloride (145) (330 mg, 1.9 mmol, 1 eq.) was stirred with KOrBu (320 mg, 2.89 mmol, 1.5 eq.) in THF overnight. CS₃ (0.6 mL, 9.5 mmol, 5 eq.) was added to give a deep-red solution. The product was isolated by column chromatography with CH₂Cl₂ to give a red oil (344 mg, 1.6 mmol, 84%). – IR (NaCl): ν = 3104, 2960, 2933, 1575, 1508, 1266, 1056, 911, 732 cm⁻¹. – 1H NMR (400 MHz, CDCl₃): δ = 6.85 (s, 2 H, NCH=CHN), 4.06 (t, J = 7.6 Hz, 2 H, NCH₂), 3.73(s, 3 H, NCH₃), 1.89–1.74 (m, 2 H, NCH₂CH₂), 1.41–1.19 (m, 2 H, NCH₂ CH₂CH₂), 0.87 ppm (t, J = 7.3 Hz, 3 H, CH₃). – 13C NMR (100 MHz, CDCl₃): δ = 224.7 (CS₂),

The reactions were carried out under argon atmosphere using standard Schlenk line techniques. Tetrahydrofuran was distilled from sodium benzenophenone ketyl. Infrared spectra were recorded on a Vector 22 FT-IR from Bruker. The absorption of solids was measured by potassium bromide pellets, the absorption of liquids by using a thin layer between sodium chloride plates. 1H and 13C NMR spectra were taken on AMX 400 (400 MHz), AC 250 P (200 MHz) or Advance 500 (500 MHz) spectrometers from Bruker. Mass spectra were recorded on a MS 5889 B instrument from Hewlett Packard. UV/Vis spectra were recorded with a Cary 50 spectrometer of Varian. The measurements were performed at 260–350 nm. The absorption maxima in betaines incorporating fluorescent moieties. Additionally, the displacement of the absorption maxima in Fig. 9 is currently under investigation.

Experimental Section

General methods

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Supporting information

A plot of the Lambert–Beer correlation is given as Supporting Information available online (DOI: 10.5560/ZNB.2014-4014).