Diffuse Reflectance Spectroscopy Applied to Solid-State 2-Methylsparteine Metal Complexes

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Diffuse reflectance spectroscopy offers a simple method to extend the measurement capabilities of UV-Vis-NIR spectroscopy to solid opaque samples, requiring minimal or no sample preparation. Owing to our interest in the photochemical properties of molecules adsorbed on solids, we have undertaken a project aimed at characterizing the spectral and analytical properties of metal complexes of 2-methylsparteine in the solid phase. In this study, we synthesized complexes between 2-methylsparteine, 2MSp, and copper and cobalt chlorides. The complexes have been characterized by UV-Vis-NIR diffuse reflectance, IR and mass spectroscopy and also by elemental analysis.

Considerable effort has been devoted to find model compounds for the metal-binding sites in a variety of systems. These studies covered different aspects of possible applications, starting from analytical determination of cations, identification of amines, through the role in living organisms, to the applications in asymmetric synthesis. The structure of sparteine, with two nitrogen atoms specifically placed in space, makes it an excellent ligand for elucidation of metal complexes [1–3]. Sparteine exhibits an interesting conformational behaviour with a number of possible conformations. This is mainly the effect of the terminal A and D rings of the alkaloid folding over the metal or folding out or a combination of both. Over a few decades several crystal structures of complexes between sparteine and copper and cobalt chlorides have been reported, and the copper(II) and cobalt(II) centres in these complexes are always found to have a distorted tetrahedral geometry [2–9].

Copper and cobalt chlorides were commercial grade supplied by POCh. The 2-methylsparteine was prepared following the procedure described in [10]. Anhydrous reagent-grade methanol was distilled from calcium hydride. Copper(II) and cobalt(II) chloride complexes were prepared by mixing methanolic solutions of copper(II) and cobalt(II) chlorides (previously dehydrated by heating at 110°C for

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several hours) and of 2-methylsparteine in stoichiometric millimolar quantities. The precipitates settled out immediately and were recrystallized from methanol. Elemental analysis was carried out by a Perkin-Elmer 2400 CHN automatic analyzer. IR spectra were recorded with a Bruker FTIR 113v spectrometer in KBr pellets. Low-resolution mass spectra were recorded using fast atom bombardment (FAB) mode on an AMD-Intectra Gmbh Model (604) two-sector mass spectrometer. Mass spectral data are reported in mass-to-charge units (m/z). Ground state diffuse reflectance absorption spectra were recorded on a Cary 5E Varian spectrophotometer equipped with an integrating sphere.

We report the synthesis and analytical properties of complexes between copper and cobalt chlorides and 2-methylsparteine as supporting ligand. The addition of copper(II) and cobalt(II) chlorides to 2-methylsparteine yields the complex. The formation of complexes is very well demonstrated in the elemental analysis and mass spectra. The results show that the complexes synthesized exhibit the 1:1 stoichiometry. This is in agreement with previous findings, which also show that number of proton sponges (including 2-methylsparteine) form the 1:1 complexes with Cu(II) cations in ethanol [11].

IR spectra of 2-methylsparteine-CuCl$_2$ and 2-methylsparteine-CoCl$_2$ complexes demonstrate the disappearance of the Bohlman "trans-band" in the vicinity of the 2840–2600 cm^{-1} IR band, as compared to the 2-methylsparteine spectrum on KBr. Fig. 1 shows the region of the IR spectra within which the carbon–hydrogen vibrational bands occur [5,12]. 2-Methylsparteine has a number of carbon–hydrogen vibrational bands in the 2800–3000 cm^{-1}, and of the low-frequency C–H stretching bands extending down to 2500 cm^{-1}, the so-called Bohlman "trans-band". It is well known that the nature of the "trans-band" depends on the conformation-configuration arrangement present in the sparteine derivatives [10]. The "trans-band" of 2-methylsparteine consists, above all, of two absorption maxima at about 2784 and 2753 cm^{-1}, which result from superposition of the oscillations of trans-axial hydrogen atoms at C-2, C-6, C-10 and C-11, C-15, C-17 respectively in relation to the lone pairs on nitrogen atoms at the N-1 and N-16 positions. The complexes between 2-methylsparteine and copper and cobalt chlorides display only bands in the 2800–3000 cm^{-1} region. Attachment of the metal to the N atoms results in the disappearance of the "trans-band" [5,6], thus, the absence of the "trans-band" in the complex suggests that both of the nitrogen atoms are coordinated. Further information about the conformation of 2-methylsparteine in these complexes may be obtained from other infrared bands. For example, the weak bands at about 416–441 cm^{-1} have been assigned to metal–nitrogen stretching oscillations [5]. However, the perturbations of the 2500–2800 cm^{-1} region are quite evident. As has been shown [10,11], the 2-methylsparteine assumes in solid phase an all-*chair* conformation with *trans* A–B and *cis* C–D, that is also the case for complexes between 2-methylsparteine and copper and cobalt chlorides (see Fig. 2).
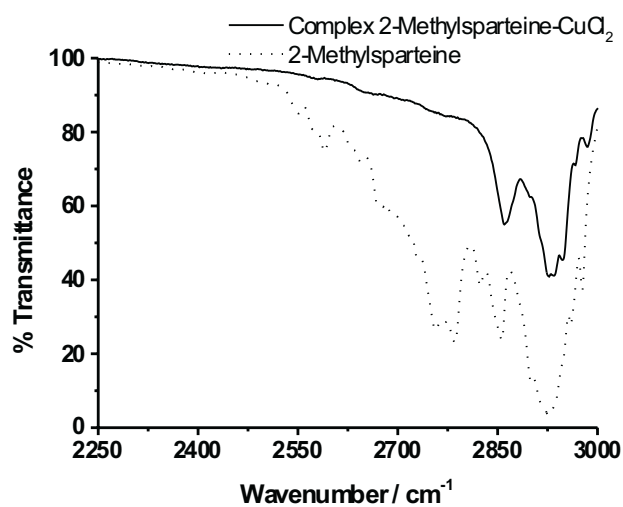
Figure 1. IR spectrum of 2-methylsparteine together with corresponding spectrum of the 2-methyl-sparteine-CuCl$_2$ complex.
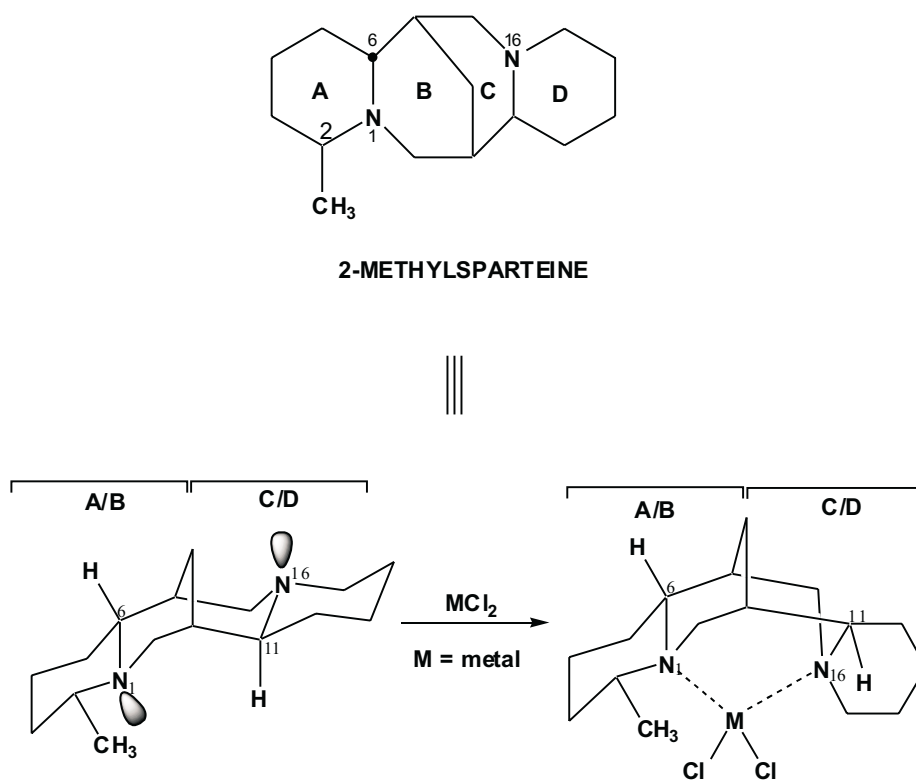

2-METHYLSPARTEINE

Figure 2. 2-Methylsparteine, 2MSp, and its metal complexes.

Presently, we were particularly interested in the feasibility of applying diffuse reflectance spectroscopy to the analysis of the copper and cobalt chlorides complexes with (−)-sparteine. A simple and successful approach, quantitatively describing the interaction of light with a diffusing sample, was proposed by Kubelka and Munk in 1931 [13,14]. In this formulation the remission function, $F(R)$, for an ideal diffuse scatterer, which is optically thick at the wavelength of choice, and for a homogeneous distribution of absorbers throughout the sample, is given by the Kubelka–Munk function *i.e.*

$$F(R) = \frac{(1-R)^2}{2R} = \frac{K}{S} \tag{1}$$

where R represents the observed diffuse reflectance from the surface of the sample K and S, being the absorption and scattering coefficients. Diffuse reflectance absorption spectra of $CuCl_2$, $CoCl_2$, 2-methylsparteine-$CuCl_2$, 2-methylsparteine-$CoCl_2$ complexes, and 2-methylsparteine itself, all taken on KBr at the loading of 2 mg/g have been recorded. Diffuse reflectance absorption spectrum of 2-methylsparteine exhibits a single absorption band with the maximum at about 218 nm. Diffuse reflectance absorption spectra of $CuCl_2$ and $CoCl_2$, together with corresponding spectra of 2-methylsparteine-$CuCl_2$ and 2-methylsparteine-$CoCl_2$ complexes, all taken on KBr at the loading of 2 mg/g, are shown in Fig. 3.

For both copper and cobalt chlorides ($CoCl_2$ and $CuCl_2$), the complexation caused significant changes in the diffuse reflectance spectra, as compared to the spectra of corresponding substrates alone. The corresponding changes can be easily seen in Fig. 3, in both UV-Vis and NIR regions. The most intriguing and obvious changes occur in the NIR region, where two new broad bands appeared. Our findings show distinct effect of complexation on spectra of not only the 2-methylsparteine-$CuCl_2$ complex but also on the spectra of 2-methylsparteine-$CoCl_2$ complex, both on solid supports.

Co(II) in tetrahedral symmetry is expected to have three spin-allowed *d-d* transitions in the Vis-NIR region, and these are from the ground state $^4A_2$ to the $^4T_1(P)$, $^4T_1(F)$, and $^4T_2(F)$ states [15]. The strong spin-orbital coupling in the tetrahedrally coordinated Co(II) complexes results in the splitting of each of the orbital crystal field terms into three spin-orbital levels [15]. The complex studied should have a distorted tetrahedral coordination sphere, similar to the complex with sparteine [2,7,8] and, thus, a spectrum close to that of a tetrahedral system. For comparison, a spectrum of tetrahedral cobalt(II) should contain visible bands at 625–500 nm ($^4A_2(F) \rightarrow {}^4T_1(P)$) transition, and the NIR bands at 3300–2500 nm and 1700–1400 nm, the respective $^4T_2(F)$ and $^4T_1(F)$ transitions [15]. The Cu(II) spectrum in pure tetrahedral crystal field should exhibit one $^2T_2 \rightarrow {}^2E_2$ spin-allowed *d-d* transition band in the NIR, which in our case is split into several components, due to the distortion of the tetrahedron to be expected due to similarity with (−)-sparteine complexes [3]. The band in the visible centred at 400 nm may be interpreted as the
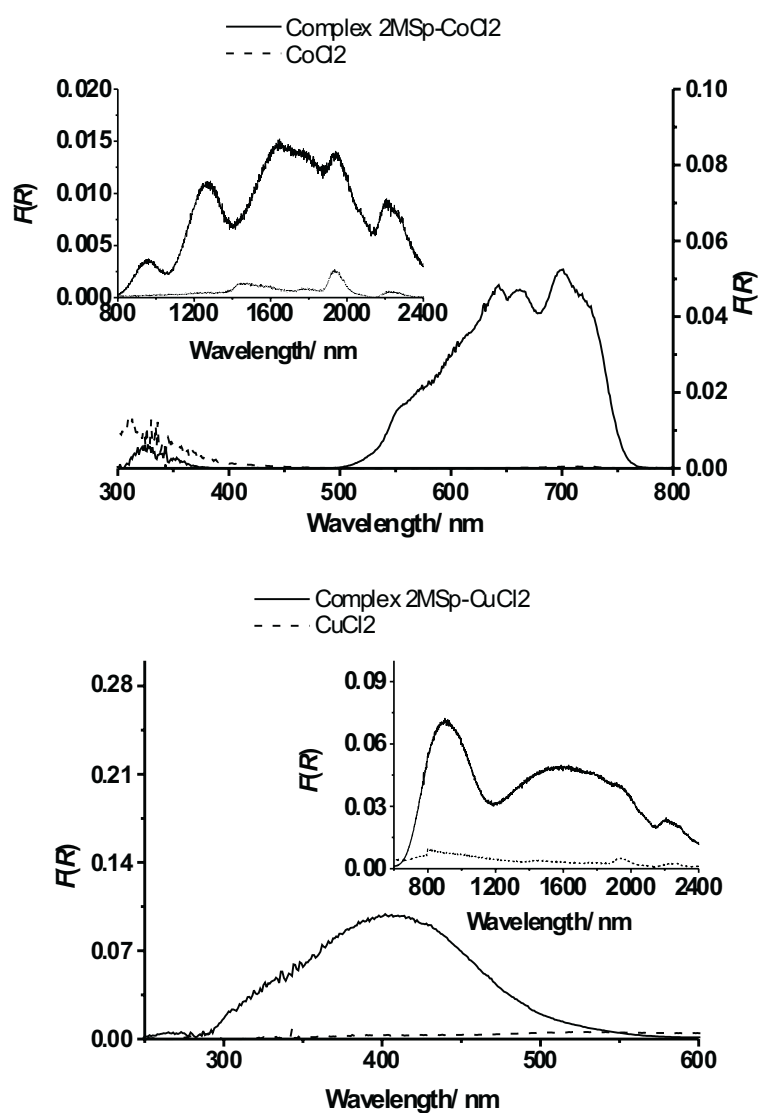
Figure 3. Ground-state diffuse reflectance absorption spectra of CoCl₂ and CuCl₂ together with corresponding spectra of 2-methylsparteine-CoCl₂ and 2-methylsparteine-CuCl₂ complexes, all spectra on KBr at the loading of 2 mg/g plotted using the Kubelka–Munk remission function $F(R)$.

LMCT band, typical for the halide ligands. The results show that diffuse reflectance spectroscopy may be used as an analytical tool to study metal organic complexes of sparteine. As a relatively cheap, fast and directly applied to solid samples, the method can be an alternative to wet studies or an additional tool to study metal organic complexes, being most important in cases when the dissolution significantly alters the complex structure and hence the UV-Vis absorption spectrum.

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