A spectroscopic and magnetic study of complexes of bis(2–benzothiazolyl)methanate and bis(2–benzoxazolyl)methanate with Co(II), Ni(II), Cu(II) and Zn(II)

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Abstract

The co-ordination geometry of the complexes M(bbtm)₂ and M(bbom)₂ (M: Co, Ni, Cu, Zn; bbtm, bis(2–benzothiazolyl)methanate; bbom, bis(2–benzoxazolyl)methanate) are discussed on the basis of their IR, Raman, resonance Raman, electronic and ESR spectra. Compounds of Ni, Co, Zn with both ligands and Cu(bbom)₂ resulted to have a distorted tetrahedral geometry. The distortion towards a square planar geometry is more marked for the M(bbtm)₂ series than for the M(bbom)₂ one. It has been impossible to suggest a co-ordination geometry for Cu(bbtm)₂, that probably has a polymeric structure. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The carbanions (hereafter indicated as bbtm and bbom) derived from bis(2–benzothiazolyl)- and bis(2–benzoxazolyl)methane, respectively (1) and (2), are two examples of N, N′-chelating ligands whose acceptor and π donor properties can be modulated by changing the electronic characteristics of the nitrogen-containing heterocycle [1].

Bis-benzothiazole compounds have been of interest for a long time, as models for the active sites of many metalloproteins and, more recently, as potential mimics for bleomycin ([2] and references therein). The benzoxazoles have been studied as models for calcimycin, but their
complexation behaviour towards transition metals is somewhat limited [2].

It is worth noting that the ligands bbtm and bbom, in addition to the two nitrogen atoms, have two oxygen or sulphur atoms which could also be potential co-ordination sites.

The purpose of the present work is to characterise two series of co-ordination compounds of formula ML2, where M is Co, Ni, Cu, Zn and L is bbtm or bbom.

The complexes of bbom are reported for the first time in this work, while those of bbtm have already been described [3]. The X-ray diffraction study of the crystal and molecular structure of Zn(bbtm)2 [3] showed that the zinc atom is co-ordinated to four nitrogen atoms in a slightly distorted tetrahedral arrangement.

2. Experimental

2.1. Preparation of compounds

The ML2 compound have been prepared by reaction of the ligand with the acetate of the desired metal (molar ratio M:L 1:2) at room temperature in methanol. An immediate formation of a precipitate was observed. After stirring for 15 min at room temperature, the precipitate was filtered, washed with methanol and dried in vacuo at a temperature lower than 60°C.

The following per cent results were found by elemental analysis (calculated values in parentheses). C30H18N4O4Co (dark red): C, 64.68 (64.64); H, 3.30 (3.26); N, 10.10 (10.05); Co, 11.0 (10.6). C30H18N4O4Cu (blue): C, 64.08 (64.11); H, 3.05 (3.22); N, 9.63 (9.97); Cu, 11.9 (11.3). C30H18N4O4Ni (dark red): C, 64.60 (64.67); H, 3.22 (3.26); N, 9.88 (10.05); Ni, 9.9 (10.5). C30H18N4O4Zn (hazel): C, 63.55 (63.9); H, 3.18 (3.22); N, 10.05 (9.94). C30H18N4S4Co (dark blue): C, 58.09 (57.96); H, 2.80 (2.92); N, 9.10 (9.01); Co, 9.80 (9.50). C30H18N4S4Cu (green): C, 57.60 (57.53); H, 2.80 (2.89); N, 8.68 (8.94); Cu, 10.8 (10.1).

The analyses of carbon, hydrogen and nitrogen were performed by means of a Perkin–Elmer 2400 elemental analyser. The percentages of metals were determined by thermogravimetric analysis using a Perkin–Elmer TGA 7 apparatus in O2 current.

2.2. IR spectra

The IR spectra in the region 4000–400 cm−1 were obtained from KBr pellets of samples by means of a Digilab FTS-40 spectrophotometer. The far-IR spectra (500–80 cm−1) were obtained from polyethylene pellets of the samples on a Digilab FTS-40 spectrophotometer equipped with a mylar beam-splitter.

2.3. Raman spectra

Raman spectra were recorded, using argon and krypton ion lasers, on a Jasco TRS-300 spectrophotometer equipped with a diode-array detector. All samples were analysed as KBr pellets. A laser power of approximately 100 mW was used.

FT-Raman spectra were recorded using a NIR laser excitation (Nd:YAG, 1064 nm) on a Bruker IFS66 spectrophotometer equipped with a Bruker FRA106 accessory. Samples were examined as powders or as KBr pellets.

2.4. Electronic spectra

Diffuse reflectance spectra in the 28 000 to 4000 cm−1 region were recorded from powder samples using a Jasco V-570 spectrophotometer equipped with a reflectance sphere. In order to detect the electronic absorptions of copper complexes located at lower energies, spectra in the range 10 000–2000 cm−1 were recorded by means of a Jasco FT-IR 800 spectrophotometer equipped with a DTGS detector and with a Specac diffuse reflectance accessory.
2.5. Magnetic measurements

Magnetic susceptibilities of the solid samples were obtained on a Cahn–Ventron RM-2 Faraday balance at room temperature, using Hg-[Co(SCN)₄]₂ for calibration.

2.6. ESR spectra

The ESR spectra of copper(II) complexes in toluene solution or as powdered samples were obtained at 123 K on a Varian-E 109 X-band spectrometer. DPPH was used as standard g-marker.

3. Results and discussion

3.1. FT-IR and FT-Raman spectra

The FT-IR spectra of M(bbtm)₂ (M = Zn, Co, Ni) complexes in the range 4000–400 cm⁻¹ resulted are very similar to one another (Fig. 1). On the contrary, the FT-IR spectrum of Cu(bbtm)₂, reported in Fig. 2, is quite different from the previous ones. The infrared data therefore suggest that at least the cobalt and nickel compounds are characterised by the same tetrahedral co-ordination of four nitrogen atoms to the metal centre, already evidenced by the X-ray structure of Zn(bbtm)₂. Similar considerations arise when comparing the FT-Raman spectra of the same complexes reported in Fig. 3. Owing to the instability of the sample with respect to the laser radiation, the Raman spectrum of Cu(bbtm)₂ could not be obtained.
FT-IR as well as FT-Raman spectra of M-(bbom)$_2$ complexes in the range 4000–400 cm$^{-1}$ (Figs. 4 and 5) are very similar to each other. The Raman spectrum of Cu(bbom)$_2$, similarly to the case of Cu(bbtm)$_2$, could not be recorded. In order to formulate hypotheses on the co-ordination geometry of the complexes formed by the ligand bbom, we synthesised the complex Pd(bbom)$_2$ following the same preparation method described for the other compounds, as preliminary X-ray diffraction measurements showed that in this compound the metal atom is co-ordinated to four nitrogen atoms in a square planar geometry. It emerged that FT-IR and FT-Raman spectra of Pd(bbom)$_2$ in the 4000–400 cm$^{-1}$ region differ substantially from those of the other compounds with the same ligand.

In the range 500–100 cm$^{-1}$ the $\nu$(M–N) stretching vibrations could be assigned. It is worth noting that, in this frequency region, the vibrational spectra show very strong analogies within each of the series of M(bbom)$_2$ and M(bbtm)$_2$ compounds for M, Zn, Ni and Co. On the contrary, in the same frequency interval, the IR spectrum of Cu(bbtm)$_2$ and the IR and Raman spectra of Pd(bbom)$_2$ differ from those of the other compounds with the corresponding ligand.

The experimental frequencies of the $\nu$(M–N) stretching vibrations, for all complexes with the exception of Cu(bbtm)$_2$, are reported in Table 1. As this table shows, for all compounds two Raman (A$_1$ and T$_2$) bands and one IR (T$_2$) band are observed, as expected in the case of a tetrahedral co-ordination geometry possibly distorted towards a planar geometry.

The far-IR spectrum of Cu(bbom)$_2$ shows a band at 311 cm$^{-1}$ that can be assigned to the $\nu$(M–N) stretching vibration of T$_2$ symmetry in a tetrahedral co-ordination geometry: even if the corresponding FT-Raman spectrum could not be obtained, this conclusion is supported by the analogies observed above between the mid-IR spectrum of this compound and those of the other complexes with the same ligand.

In the FT-IR spectrum of Cu(bbtm)$_2$, too, we observed a strong band at 283 cm$^{-1}$ that can be
Table 1
Frequencies (cm\(^{-1}\)) of the \(\nu(M-N)\) stretching vibrations of the complexes \(M(bbtm)_2\) and \(M(bbom)_2\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR</th>
<th>Raman</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn(bbtm)(_2)</td>
<td>287(^\text{vs})</td>
<td>290(^\text{m})</td>
</tr>
<tr>
<td>Co(bbtm)(_2)</td>
<td>316(^\text{vs})</td>
<td>320(^\text{m})</td>
</tr>
<tr>
<td>Ni(bbtm)(_2)</td>
<td>318(^\text{vs})</td>
<td>318(^\text{m})</td>
</tr>
<tr>
<td>Zn(bbom)(_2)</td>
<td>309(^\text{vs})</td>
<td>313(^\text{m})</td>
</tr>
<tr>
<td>Co(bbom)(_2)</td>
<td>337(^\text{vs})</td>
<td>339(^\text{m})</td>
</tr>
<tr>
<td>Ni(bbom)(_2)</td>
<td>337(^\text{vs})</td>
<td>343(^\text{m})</td>
</tr>
<tr>
<td>Cu(bbom)(_2)</td>
<td>311(^\text{vs})</td>
<td>289(^\text{m})</td>
</tr>
</tbody>
</table>

\(^\text{vs}\) Very strong.
\(^\text{m}\) Medium.

Table 2
Magnetic moment \(\mu_{\text{eff}}\) (B.M.) at room temperature of the complexes \(M(bbtm)_2\) and \(M(bbom)_2\).

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Metal</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>bbtm</td>
<td>4.52</td>
<td>3.33</td>
<td>1.34</td>
<td></td>
</tr>
<tr>
<td>bbom</td>
<td>4.60</td>
<td>3.20</td>
<td>1.73</td>
<td></td>
</tr>
<tr>
<td>(^\text{a})</td>
<td>4.3–4.5</td>
<td>3.42–3.55</td>
<td>2.28–2.13</td>
<td></td>
</tr>
</tbody>
</table>

\(^\text{a}\) Values for the magnetic moments of tetrahedral complexes of the metals with \(N,N'\)-chelating ligands [4].

ascribed to a \(\nu(M-N)\) stretching vibration, but, as the corresponding Raman spectrum was not obtained, it was again impossible to put forward hypotheses on the co-ordination geometry of this compound.

3.2. Magnetic and ESR measurements

Values for the magnetic moments, as calculated from the experimental data on magnetic susceptibilities, are reported in Table 2 along with those of other tetrahedral metal complexes of \(N, N'\)-chelating ligands [4].

It is worth noting that the magnetic moment values listed in Table 2 are in good agreement with those reported in the literature, with the exception of the value obtained for Cu(bbtm)\(_2\), which resulted much lower than that expected for a tetrahedral co-ordination.

From the ESR spectrum of the toluene solution of Cu(bbom)\(_2\) (Fig. 6) we obtained the following values of the spectromagnetic parameters: \(g|| = 2.22; g\perp = 2.06; A|| (\text{Cu}) = 154 \times 10^{-4} \text{ cm}^{-1}\). It is worth observing that the value of \(A||\) is intermediate [5] between that expected for a tetrahedral co-ordination (about \(110 \times 10^{-4} \text{ cm}^{-1}\)) and that expected for a square planar one (about \(200 \times 10^{-4} \text{ cm}^{-1}\)). Each of the four signals in the \(g||\) region shows nine components due to the superhyperfine coupling of the unpaired electron with the four nitrogen nuclei. On the other hand, the perpendicular component of the resonance is splitted in fourteen signals arising from the superposition of the four hyperfine lines due to the coupling with the copper nucleus and the nine superhyperfine lines due to the four nitrogen nuclei.

On the contrary, the ESR spectra of Cu(bbtm)\(_2\), both in solution and in the solid state, show very weak and broad signals, as expected if considering the value of the magnetic moment of this compound. One should probably take into account the presence of an antiferromagnetic coupling among copper atoms of different molecules for Cu(bbtm)\(_2\).
From the diffuse reflectance electronic spectra of the complexes (Figs. 7–9) the frequency values of the absorption maxima reported in Table 3 were obtained.

The electronic spectra of the nickel and cobalt compounds showed the patterns expected [4,6,7] for compounds with distorted tetrahedral MN₄ chromophores. The corresponding assignments of the absorption bands are also reported in Table 3.
Moreover, taking into account the splitting of the bands connected to degenerate energy levels, we could deduce that the bbtm complexes are more distorted from the tetrahedral co-ordination than those of bbom.

In order to interpret the electronic spectra of the copper complexes it was necessary to consider that, for the $d^9$ configuration, the square planar co-ordination is preferred to the tetrahedral one. Consequently, copper compounds often assume a distorted tetrahedral co-ordination having $D_{4d}$ symmetry which maintains the degeneration of the $d_{xz}$ and $d_{yz}$ orbitals and for which three electronic transitions are expected from $2B_2$ ground state towards $2E$, $2B_1$, and $2A_1$ excited states. We observed that, while the electronic spectrum of Cu(bbom)$_2$ is consistent with what expected for a copper (II) complex containing a distorted tetrahedral chromophore CuN$_4$, the spectrum of Cu(bbtm)$_2$ shows some peculiar aspects. In fact, for Cu(bbom)$_2$ (Fig. 9b) a band is observed at 6000 cm$^{-1}$, which is in agreement with the crystal field value expected for a distorted tetrahedral co-ordination [8]. Moreover, the presence of a band at about 15000 cm$^{-1}$ pointed out that the CuN$_4$ chromophore of this compound has a distorted tetrahedral geometry with a dihedral angle of about 58° [6,9–11]. On the contrary, the electronic spectrum of Cu(bbtm)$_2$ (Fig. 9a) was quite difficult to interpret principally because of the presence of a band at about 4000 cm$^{-1}$, since this value, according to the literature, is lower than that expected even for a tetrahedral co-ordination.

### 3.4. Resonance Raman spectra

Aiming to a better assignment of the electronic spectra, we recorded the resonance Raman spectra (hereafter indicated as RR spectra) on the solid samples using the following excitation lines: 457.9 and 514.5 nm (corresponding respectively to 21 839 and 19 426 cm$^{-1}$) of an argon ion laser, 647.1 nm (15 453 cm$^{-1}$) of a krypton ion laser and 1064 nm (9400 cm$^{-1}$) of a Nd:YAG laser.

The attribution of the spectra of M(bbtm)$_2$ complexes was obtained taking into account the data reported in the literature for benzothiazole and its derivatives [12,13] and for bis(2–benzothiazolyl)methane and its derivatives [14]. Consequently we assigned the bands at 1587, 1575 (shoulder) and 1485 cm$^{-1}$ to the so-called I, II, and III vibrations of the thiazo group [13,14] and the band near 1450 cm$^{-1}$ to a ring vibration [14]. The bands between 1310 and 1000 cm$^{-1}$ can be attributed to the in-plane $\delta$(CH) deformations of the aromatic ring and to the skeletal vibrations of benzothiazole [12]. Finally, in the range 1000–500 cm$^{-1}$ we find bands that can be assigned to the out of plane $\gamma$(CH) deformation vibrations of the aromatic ring and the out-of-plane skeletal vibrations of benzothiazole [12]. The assignments of the RR spectra were completed utilizing the values of the $\nu$(M–N) stretching vibrations obtained from far-IR and FT-Raman spectra.

Comparing the Raman spectrum of Zn(bbtm)$_2$ recorded by using the 1064 nm exciting line with that excited by the 514.5 nm line (Fig. 10), we find in the second spectrum an intensity enhancement of the signals due to total symmetric modes of the ligand with respect to bands assigned to less symmetric modes and to metal-ligand stretching vibrations. This fact suggest that the 514.5 nm line produced a pre-resonance condition relatively to an electronic transition internal to the ligand: in fact, its protonated form, bbtmH, reaches its maximum absorption in the solid state at about 400
Fig. 11. Raman spectra of Co(bbtm)₂ with excitation at: (a) 457.9 nm; (b) 647 nm; and (c) 1064 nm obtained from KBr pellets.

Fig. 12. Raman spectra of Ni(bbtm)₂ with excitation at: (a) 457.9 nm; (b) 647 nm; and (c) 1064 nm obtained from KBr pellets.

nm. Owing to a strong fluorescence emission, however, it was not possible to obtain a Raman spectrum for the Zn complex at 457.9 nm.

With regard to the RR spectra of Co(bbtm)₂ (Fig. 11), we note that, on passing from the 1064 nm to the 647 nm exciting line, the relative intensities of the ligand bands begin to show changes similar to those observed for Zn(bbtm)₂, that are completely developed only in the spectrum excited at 457.9 nm. Consequently the electronic bands at 16 571 and 8800 cm⁻¹ must be assigned exclusively to d-d transitions. The intensity variations are due to a preresonant effect connected with the electronic band of the ligand observed at 400 nm, with which the 457.9 nm line produces a resonance condition.

The RR spectra of Ni(bbtm)₂ are presented in Fig. 12 and show a quite different pattern with respect to those of the cobalt compound. In fact, by using the 647 nm excitation line we obtained the enhancement of the bands at 258 cm⁻¹, due to a metal-nitrogen stretching vibration, at 1588 and 1465 cm⁻¹, typical of the thiazole moiety of the ligand, and at 500 cm⁻¹, also due to a vibration of the benzothiazole skeleton. The assignments of the enhanced bands indicate that the electronic band of Ni(bbtm)₂ which appears at 15357 cm⁻¹ has a partial character of a charge-transfer transition. The RR spectrum excited by the 457.9 nm line shows the same pattern observed for the cobalt complex, suggesting that the electronic bands with wavenumbers greater than 20000 cm⁻¹ are due for both complexes to internal transitions of the ligand.

As regards Cu(bbtm)₂, we could obtain the RR spectrum only with the 457.9 nm excitation line. Therefore we were not able to derive any useful information concerning this complex even from RR spectroscopy. As a matter of fact, we were only able to note that the RR spectrum of Cu(bbtm)₂ shows a completely different pattern from those of the other compounds of the same ligand.

In the Raman spectra of the compounds M-(bbom)₂ it was possible to observe characteristic bands of the oxazolic unit at 1628, 1613 and 1565 cm⁻¹ [13]. On the basis of the assignment reported in the literature [15] for the derivatives of
benzoxazole substituted in position 2, most of the bands located between 1550 and 1000 cm$^{-1}$ have been attributed to in-plane deformation vibrations of the C–H bonds and the benzoxazole skeleton. Below 1000 cm$^{-1}$ also bands due to out-of-plane deformation modes are observed.

We were able to obtain the RR spectra of all complexes of the bbom ligand with the exception of Zn(bbom)$_2$ owing to the fluorescent behaviour of this compound. For Cu(bbom)$_2$ the FT-Raman spectrum is not available, so rendering less accurate the comparison of the relative intensities of the bands.

The RR spectra of Co(bbom)$_2$, Ni(bbom)$_2$ and Cu(bbom)$_2$ excited by the 457.9 nm line (Figs. 13–15) show an intensity enhancement of some of the ligand bands. On the contrary, the RR spectra for Ni(bbom)$_2$ and Cu(bbom)$_2$ excited by the 647 nm line exhibit a remarkable enhancement of the bands due to the metal-ligand stretching vibrations and to the vibrational modes of the oxazolic unit, while the RR spectrum of Co(bbom)$_2$ excited at 514.5 nm does not show any enhancement of the bands associated with metal-ligand bonds. So we are led to think that the absorption bands of Ni(bbom)$_2$ at about 15 000 cm$^{-1}$ and of Cu(bbom)$_2$ at 15 428 cm$^{-1}$ must be partially due to a charge-transfer mechanism, while the 18 071
cm\(^{-1}\) absorption band of Co(bbom)\(_2\) has presumably pure \(d-d\) character; at the same time, the electronic bands of all three complexes above 20 000 cm\(^{-1}\) can be assigned to internal transitions of the ligand.

It is worth noting that, while the electronic spectra of the Ni complexes are very similar to each other, Co(bbom)\(_2\) exhibits quite different absorption maxima from those of Co(bbtm)\(_2\). This fact is in good agreement with the above suggested assignments of the electronic bands for these compounds. Indeed, \(d-d\) transitions (predominant in the Co case) are more sensitive than charge-transfer ones (more relevant in the Ni case) to the distortion of the co-ordination geometry of the metal ion.

4. Conclusions

The results previously described pointed out that the M(bbtm)\(_2\) compounds of nickel, cobalt and zinc have a co-ordination tetrahedral geometry, though distorted toward a square planar one.

This conclusion was supported by IR and Raman spectra and by diffuse reflectance spectra in the visible region, with regard to nickel and cobalt complexes. It has been impossible to suggest a co-ordination geometry for Cu(bbtm)\(_2\). It is certainly true that this compound has a co-ordination geometry completely different from those of all other compounds of the same ligand. This copper complex might show interactions between the copper atom of one molecule and the sulphur atom of another. Such interactions would explain the very weak signals observed in the ESR spectrum and the low value of the magnetic moment of this compound. As a matter of fact the suggested interaction would cause magnetic coupling among copper(II) ions of different molecules.

As demonstrated by the IR and Raman spectra, the electronic spectra, as well as the ESR spectrum for Cu(bbom)\(_2\), all compounds of formula M(bbom)\(_2\) show a tetrahedral co-ordination geometry, always distorted towards square planar, even if to a lesser extent than bbtm derivatives.

It is remarkable that a detailed assignment of the electronic spectra has been possible only on the basis of the RR data.

References