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Synthesis and structure of novel benzisothiazole-tetrazolyl derivatives for potential application as nitrogen ligands

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ABSTRACT

The synthesis and characterization of novel benzisothiazole-tetrazolyl derivatives differing on the spacer-group used for the linkage of two heterocycles are described. The application of these compounds as nitrogen ligands for coordination with transition metals was also explored, leading to the preparation of *3-[1-(2-1H-tetrazol-5-yl)ethoxy]-1,2-benzisothiazole 1,1-dioxide-Mn(II) and N-(1,1-dioxo-1,2-benzisothiazol-3-yl)-amine-1H-tetrazole-Mn(II) complexes*.

1. Introduction

Tetrazoles and benzisothiazoles have received much attention due to their important practical applications in major areas, such as medicine and agriculture.

In the last decade, a significant part of the research carried out in our laboratories has been directed to the investigation of structure–reactivity correlations in tetrazole- and benzisothiazole-based compounds, aiming at the development of new synthetic methodologies. For instance, ethers derived from tetrazole and benzisothiazole have important synthetic uses as intermediate compounds for reductive cleavage of the C–O bond, in phenols and alcohols. These ethers are easily obtained from reaction of the corresponding hydroxylic compound with commercially available 5-chloro-1-phenyl-(1*H*)-tetrazole or with 3-chloro-1,2-benzisothiazole 1,1-dioxide. The electron-withdrawing tetrazolyl or benzisothiazolyl system, together with oxygen from the original alcohol, represents an efficient nucleofuge in heterogeneous transfer hydrogenolysis catalyzed by transition metals [1–4]. Much of the reactivity of these ethers can be ascribed to changes in bond lengths about the central C_{HAR}–O–C_A ether bonds (HAR = heteroaromatic ring and A = allyl, benzyl, naphthyl or aryl group), caused by the powerful electron-withdrawing effect of the tetrazolyl- or *pseudo*-saccharyl ring system. Therefore, the originally strong C_A–O bond in the hydroxylic compound becomes weak, and the bond between the oxygen and the carbon of the heteroaromatic ring (C_{HAR}–O) becomes very strong [5]. In allyl- and alkyl-, tetrazolyl- and *pseudo*-saccharyl ethers, the net result of the electronic changes is also important, in that it provides a molecular structure that lies close to a transition state structure in which the originally strong C_A–O bond in the ether becomes easily cleavable to give the thermally isomerised N-allyl- or N-alkyl-tetrazolones or benzisothiazolones, through Claisen- or Chapman-like rearrangements [6–11]. N-allyltetrazolones revealed to be important starting compounds for the easy preparation of new 2,3-dihydro-pyrimidinones [12,13].

In recent years, the design of new bridging ligands for controlling the molecular architectures required for defining specific physical properties in resulting coordination compounds has been a topic of research for many research groups, in major fields such as supramolecular chemistry [14] and molecular magnetism [15].

The heterocycle tetrazole has recently found applications in coordination chemistry, as a ligand [16,17]. Of interest to supramolecular chemists is the coordination ability of the tetrazolyl ligand through four nitrogen electron-donating atoms that allows it to serve as a multidentate or as a bridging building block in supramolecular assemblies. Indeed, it has been shown that the tetrazole ligand is able to participate in at least seven distinct types of coordination modes with metal ions, in the construction of novel metal–organic frameworks. Furthermore, numerous tetrazolyl ligands, coordinated with different metal centres, such as nickel, ruthenium, palladium or platinum, have been tested in catalyzed reactions [18–20].

Similarly, the diversity of bonding modes adopted by the 1,2-benzisothiazole-3-one 1,1-dioxide anion (deprotonated saccharin) and the fortuitous crystalline nature of the resulting complexes appear to be excellent reasons to scrutinize this system. As a polyfunctional ligand, deprotonated saccharin can exist as anion or can be incorporated into a complex as a ligand, and it can also

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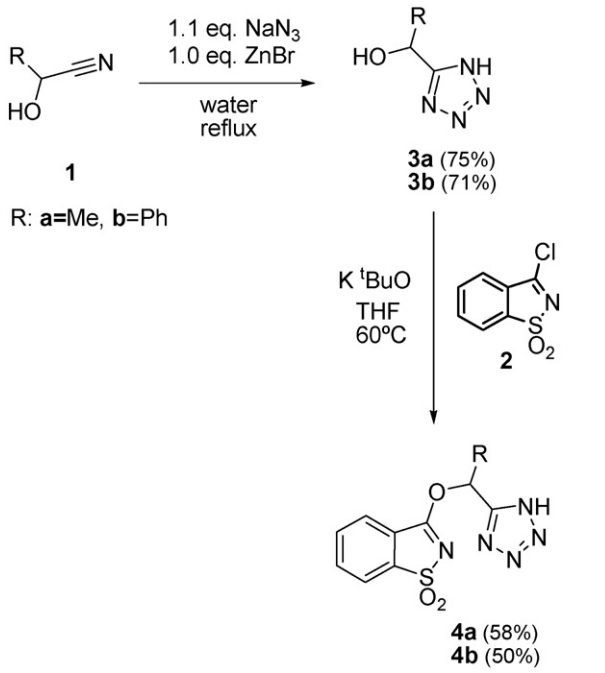
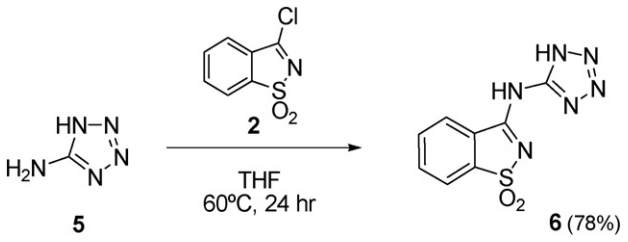


Scheme 1.



Scheme 2.

co-exist simultaneously as ionic and coordinated species in the same structure. As a ligand, it can be engaged in N, O(C=O) or O(SO_2) coordination, but can also act as a bidentate amidato-like bridging agent [21–23]. The saccharinate anion interacts with metal centres in various ways, generating relatively strong interactions in crystalline environments, mostly through hydrogen bonding.

Although several tetrazole derivatives and saccharinate anion have demonstrated the ability to bind cations of transition metals individually, they have not been investigated together as ligands. Taking advantage of our experience concerning the synthesis and reactivity of tetrazole- and benzisothiazole-based compounds, we have devised synthetic routes to benzisothiazole-tetrazolyl derivatives with the final aim of investigating their application as nitrogen ligands for coordination with transition metals. Accordingly, it was decided to synthesize novel potential benzisothiazole-tetrazolyl nitrogen ligands, differing on the spacer-group used for the linkage of two heterocycles (see Schemes 1 and 2). In this publication, we report on the synthesis and characterization of three new benzisothiazole-tetrazolyl derivatives, and their complexation with metals.

2. Experimental

2.1. Computational details

Quantum chemical calculations for the derivatives **4a** and **6** were performed with the Gaussian 03 program package [24] at the DFT level of theory, using the 6-31G(d,p) basis set and the three-parameter density functional, abbreviated as B3LYP, which includes Becke's gradient exchange correction [25] and the Lee, Yang, Parr correlation functional [26]. No symmetry restrictions were imposed on the initial structures.

2.2. Synthesis

2.2.1. 3-Chloro-1,2-benzisothiazole 1,1-dioxide (*2*)

The experimental procedure used has been reported previously [27]. From saccharin (10.2 g; 56 mmol), and phosphorus pentachloride (14.0 g; 66 mmol) heated at 180 °C. Colourless needles from trichloromethane (7.00 g; 63% yield), mp 143–145 °C (lit. 143–145 °C [27]). IR ν_{max} (cm^{-1}): 1724, 1654, 1603 (C=C), 1346 (SO_2), 775 (Ar–H) and 692 (C–Cl); ^{1}H NMR ($CDCl_3$): δ 7.85 (4H, m, Ar–H). Found: C, 41.5%; H, 2.0%; N, 6.9%; Calcd for $C_7H_4NO_2SCl$: C, 41.7%; H, 2.0%; N, 7.0%. MS (EI), *m*/*z* 201 $[M]^+$.

2.2.2. 1-(1H-Tetrazol-5-yl)ethanol (*3a*)

Sodium azide (1.43 g; 22 mmol), zinc bromide (4.50 g; 20 mmol), 2-hydroxy-propanenitrile (1.45 mL; 20 mmol) and water (50 mL) were mixed in a 250-mL round-bottomed flask and the mixture was stirred under reflux for 20 h. After cooling, hydrochloric acid (3N; 30 mL) and ethyl acetate (100 mL) were added, and vigorous stirring was continued until no solid was present and the aqueous layer attained a pH of 1. The organic layer was separated and the aqueous layer extracted with ethyl acetate (2× 50 mL). The combined organic layers were evaporated, aqueous NaOH (0.25 M; 200 mL) was added to the residue, and the mixture stirred for 30 min, until the original precipitate was dissolved and a suspension of zinc hydroxide was formed. The suspension was filtered, and the solid washed with aqueous NaOH (1 M; 20 mL). Hydrochloric acid (3N; 40 mL) was added to the filtrate with vigorous stirring causing the separation of oil. After the addition of a saturated solution of NaCl (brine), the aqueous layer was extracted with ethyl acetate (3× 100 mL). The combined organic layers were dried over anhydrous sodium sulphate and evaporated to afford the final product as a white amorphous powder (1.70 g; 75% yield). IR ν_{max} (cm^{-1}): 3390 (OH), 1696, 1624, 1243, 1123; ^{1}H NMR ($CDCl_3$): δ 7.55 (br, 1H), 7.22–7.35 (q, 1H), 7.35 (d, 3H); MS (EI), *m*/*z* 115 (33%) $[M+H]^+$, *m*/*z* 132 (100%) $[M+NH_4]^+$. Acc. Mass (CI): Found, 115.1145; Calcd for $C_3H_7N_4O$, 115.1134.

2.2.3. Phenyl(1H-tetrazol-5-yl)methanol (*3b*)

Preparation of this compound followed a modified version of a procedure reported previously [28]. From sodium azide (1.43 g; 22 mmol), zinc bromide (4.50 g; 20 mmol), 2-hydroxy-2-phenylacetonitrile (2.66 g; 20 mmol) and water (60 mL). The reaction mixture was refluxed for 18 h with vigorous stirring. Extraction, as described above for derivative **3a**, afforded the required product as a colourless solid (2.5 g; 71% yield), mp 176–177 °C (lit. [28] 178–179 °C). IR ν_{max} (cm^{-1}): 3445 (OH), 2589, 1699, 1434, 1251, 1040; ^{1}H NMR ($CDCl_3$): δ 7.47 (m, 2H), 7.35 (m, 2H), 7.30 (m, 1H), 6.81 (br, 1H), 6.15 (s, 1H); MS (EI), *m*/*z* 178 (91%) $[M+2H]^+$, *m*/*z* 194 (100%) $[M+NH_4]^+$.

2.2.4. 3-[1-(2-1H-Tetrazol-5-yl)ethoxy]-1,2-benzisothiazole 1,1-dioxide (*4a*)

A mixture of 1-(1*H*-tetrazol-5-yl)ethanol (0.20 g; 1.75 mmol), 3-chloro-1,2-benzisothiazole 1,1-dioxide (0.35 g; 1.75 mmol) and a suspension of potassium tert-butoxide (0.65 g; 5.25 mmol) in dry THF (50 mL) was stirred at 60 °C under a nitrogen atmosphere, until TLC analysis (DCM/toluene 3:1) indicated the absence of starting material (48 h). The excess of base was filtered off and then ethyl acetate (100 mL) was added to the reaction mixture. The crude was washed with diluted hydrochloric acid (1 M; 3× 50 mL), brine (3×

50 mL) and finally dried over anhydrous sodium sulphate. Evaporation of the solvent under reduced pressure and recrystallisation from a mixture of toluene/dichloromethane (3:2) afforded compound **4a** as a amorphous pale yellow powder (0.28 g; 58% yield), mp 210–211 °C. IR ν_{max} (cm^{-1}): 3091, 2974, 1721, 1593, 1463, 1336 (SO_2), 1177; ^1H NMR ($CDCl_3$): δ 8.05–8.08 (d, 1H), 7.91–7.95 (m, 2H), 7.86–7.90 (d, 1H), 5.26 (1H, d), 1.39–1.41 (d, 3H); MS (EI), *m/z* 279 $[M]^+$; Acc. Mass (CI): Found = 280.1089, Calcd for $C_{10}H_{10}N_5O_3S$: 280.1022.

2.2.5. 3-[(2-1H-Tetrazol-5-yl)benzyloxy]-1,2-benzisothiazole 1,1-dioxide (**4b**)

The procedure adopted for the preparation of compound **4b** was similar to that described above for compound **4a**. From phenyl(1*H*-tetrazol-5-yl)methanol (0.28 g; 1.50 mmol), 3-chloro-1,2-benzisothiazole 1,1-dioxide (0.30 g; 1.50 mmol) and a suspension of potassium tert-butoxide (0.55 g; 4.50 mmol) in dry THF (50 mL), stirred at 60 °C for 72 h. Compound **4b** was obtained as a light yellow solid (0.26 g; 50% yield), mp 171–173 °C. IR ν_{max} (cm^{-1}): 3091, 2974, 1722, 1686, 1453, 1336 (SO_2), 1177, 920, 758, 708; ^1H NMR ($CDCl_3$): δ 8.67–8.70 (d, 1H), 8.08–8.13 (m, 2H), 8.05–8.08 (d, 1H), 7.89–7.93 (m, 2H), 7.55–7.63 (m, 2H), 7.46–7.51 (t, 1H), 6.13(s, 1H); MS (EI), *m/z* 342 $[M+H]^+$; Acc. Mass (CI): Found, 342.2019; Calcd for $C_{15}H_{11}N_5O_3S$: 342.2131.

2.2.6. N-(1,1-dioxo-1,2-benzisothiazol-3-yl)-amine-1H-tetrazole (**6**)

A mixture of commercial anhydrous 5-aminotetrazole (Sigma–Aldrich; 0.22 g; 2.56 mmol) and 3-chloro-1,2-benzisothiazole 1,1-dioxide (0.53 g, 2.56 mmol) in dry THF (20 mL) was stirred at 60 °C for 24 h under a nitrogen atmosphere. The solvent was then evaporated under reduced pressure and the remaining solid was washed with acetone, dried under vacuum at room temperature and recrystallised from a mixture of acetone/ethanol (1:1) to give the required product as a colourless powder (0.5 g; 78% yield), mp 270–271 °C. IR ν_{max} (cm^{-1}): 3221 (NH), 3091, 1608, 1542, 1430, 1323 (SO_2), 1172, 1037, 951; ^1H NMR (DMSO): δ 8.49–8.54 (m, 1H), 8.10–8.13 (m, 1H), 7.91–7.96 (m, 2H), 2.51 (s, 1H); MS (EI), *m/z* 251 (17%) $[M+H]^+$; Acc. Mass (CI): Found = 251.2010, Calcd for $C_8H_6N_6O_2S$: 251.2018.

2.3. Preparation of complexes

2.3.1. 3-[1-(2-1H-Tetrazol-5-yl)ethoxy]-1,2-benzisothiazole 1,1-dioxide-Mn(II) complex (**7**)

A mixture of ligand **4a** (0.10 g; 0.36 mmol) and manganese(II) acetate tetrahydrate (0.09 g; 0.36 mmol) in ethanol (10 mL) was stirred at room temperature for 24 h. Then the brown precipitate (resulting from degradation of ligand and manganese acetate complex) was filtered off and the remaining solution evaporated under reduced pressure, at room temperature, to afford the required product as a pale yellow solid (0.11 g; 68% yield). Acc. Mass (ES+): Found = 475.0053, Calcd for $C_{14}H_{15}N_5O_7SNaMn$: 474.9970.

2.3.2. N-(1,1-dioxo-1,2-benzisothiazol-3-yl)-amino-1H-tetrazole-Mn(II) complex (**8**)

A mixture of ligand **6** (0.10 g; 0.40 mmol) and manganese(II) acetate tetrahydrate (0.1 g; 0.40 mmol) in ethanol (10 mL) was stirred at room temperature for 24 h. Then, the pale precipitate (resulting from degradation of ligand and manganese acetate complex) was filtered off and the remaining solution evaporated under reduced pressure (RT). The required product was obtained as a colourless solid (0.107 g; 63% yield). Acc. Mass (ES+): Found = 446.0013, Calcd for $C_{12}H_{12}N_6O_6SNaMn$: 445.9805.

3. Results and discussion

The synthetic methodologies adopted to produce the benzisothiazole-tetrazolyl derivatives are presented in Schemes 1 and 2. The synthesis of the hydroxyalkyl-tetrazoles **3a** and **3b** was performed in water, following a methodology similar to that developed by Demko and Sharpless [28,29].

Compounds **4a** and **4b** were prepared by reaction of the corresponding hydroxyalkyl-tetrazole (**3a** and **3b**) with *pseudo*-saccharyl chloride, in the presence of base. The reaction yields achieved for the synthesis of these two derivatives are similar to those obtained for a large range of nucleophilic substitution reactions with *pseudo*-saccharyl chloride, involving different alcohols [3,4,10].

The procedure adopted for the synthesis of derivative **6** involves reaction of 5-aminotetrazole with saccharyl chloride in dry THF. The required 5-saccharylamino-1*H*-tetrazole **6** was obtained in a good yield (78%).

In order to obtain some relevant structural data on the synthesized molecules (**4a**-**b**, and **6**), DFT(B3LYP)/6-31G(d,p) calculations were carried out for derivatives **4a** and **6**. These derivatives have three and two internal rotational degrees of freedom respectively, which may result in the existence of different conformers. However, a complete conformational study of both compounds was not carried out during this work. The two conformers selected, presented in Fig. 1, are those that were predicted to possess the most suitable geometry for coordination of both tetrazole and benzisothiazole nitrogen atoms with transition metals [16]. In both optimized structures of derivatives **4a** and **6**, the two heterocyclic

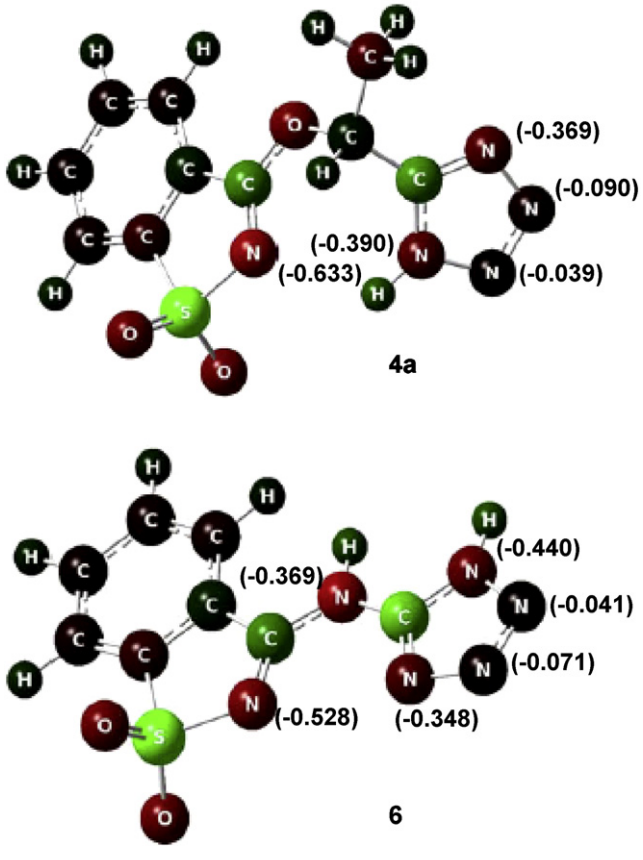
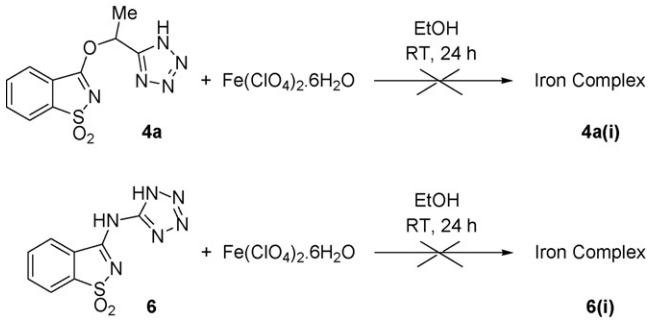


Fig. 1. B3LYP/6-31G(d,p) optimized structures of derivatives **4a** and **6**. Selected Mulliken atomic charges (a.u.) of nitrogen atoms are showed in parentheses. Colour atoms by charge with force symmetric charge range (red: atoms with positive partial charge; green: atoms with negative partial charge). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)



Scheme 3.

systems (tetrazole and benzisothiazole) have approximately planar geometries. However, only for derivative **6** these two moieties share the same plane. The angle between the tetrazole ring and the benzisothiazolyl system on derivative **4a** was predicted by the calculations to be ca. 110°. Certainly, structural differences on the 1,2-benzisothiazolyltetrazoles, bearing an amino or ether linkage, will play a role in determining their coordination behaviour with transition metals. However, the rotational freedom of the tetrazolic moiety in relation to the benzisothiazolyl system allows us to expect that compounds **4a**-**b** and **6** can adopt a conformation with the required orientation of the two ring units for formation of metal complexes.

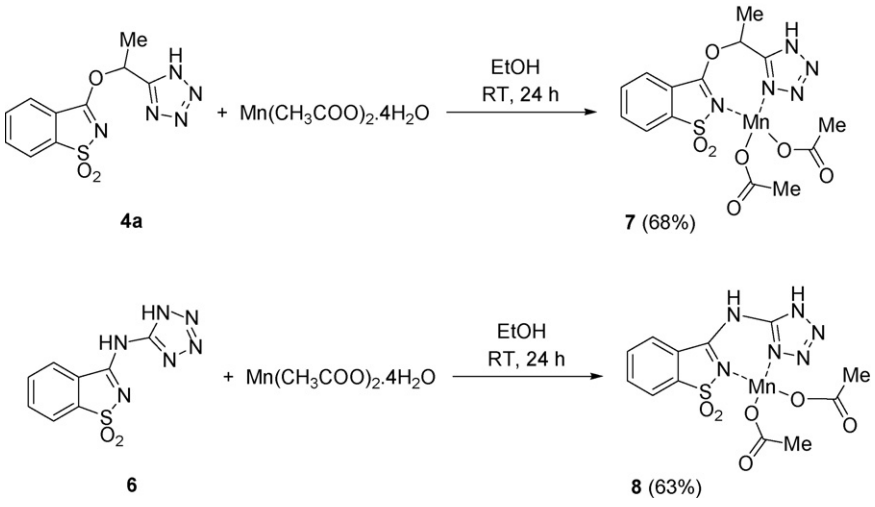
Partial negative charges on nitrogen atoms of **4a**-**b** and **6** are also shown in Fig. 1. The relatively high values of these charges in two of the nitrogen atoms of the tetrazolyl ring and in the nitrogen atom of benzisothiazolyl system (see Fig. 1) suggest that these atoms bear the capacity for charge donation and, therefore, the ability to form coordination bonds with transition metals. Preliminary complexation reactions involving derivatives **4a** and **6** as potential multidentate nitrogen ligands, with manganese(II) and iron(II) complexes are now discussed. Because of their potential interest of Fe(II) spin-crossover coordinating materials [15] the two derivatives were first tested as nitrogen ligands in reactions with an iron(II) complex. The procedure adopted in the synthesis involved vigorous stirring of **4a** or **6** with the iron(II) perchlorate complex, $Fe(ClO_4)_2{\cdot}6H_2O$, in equimolar amounts, at room temperature, in ethanol. However, product analysis indicated that no complex associating iron and derivatives **4a** or **6** had been formed (Scheme 3).

Mass spectrometry confirmed the occurrence of degradation of ligands **4a** and **6** during reaction, inferred by the presence of molecular ion peaks corresponding to isolated saccharin. Thus, in the reaction conditions used, both compounds are susceptible to nucleophilic attack on the sp^2 imino carbon of the benzisothiazolyl system, and the reaction might be accelerated in the presence of perchlorate salts, if the mechanism operating is sensitive to the solvent ionizing power [30]. Degradation of the two potential ligands possibly induced by the oxidative nature of the perchlorate ligand, can explain the failure on coordination of iron(II) with the benzisothiazole-tetrazolyl derivatives. Analysis of the literature also revealed that coordination of ditetrazole ligands with Fe(II) is not always feasible, depending largely on the structure of the bridge connecting the two heterocycles [31]. In our case, one tetrazolyl ring is replaced by a benzisothiazolyl structure, but the difficulties appear to be the same.

Derivatives **4a** and **6** were stirred with the manganese(II) acetate tetrahydrate complex, $Mn(CH_3COO)_2{\cdot}4H_2O$, in ethanol. The experimental procedure adopted in these reactions was identical to that used in the attempted preparation of the iron(II) complexes (see Scheme 4). However, in this case, after solvent evaporation, an amorphous pale yellow powder was obtained from complexation of derivative **4a** with Mn(II), and a white powder from complexation of derivative **6** with the same metal cation. Product analysis attested the presence of coordination complexes between manganese and both derivatives. Structures **7** and **8**, represented in Scheme 4, were proposed for the final products.

Mass spectra of compound **8** were obtained using electrospray as the ionization technique. Interestingly, in the positive mode, using methanol as solvent, peaks corresponding to molecular ions of 336, 368 and 400 were found. These peaks clearly indicate the formation of complexes involving ligand **6** with Mn plus one methoxide (*m*/*z*: 336), ligand **6** with Mn plus methoxide and one molecule of methanol (*m*/*z*: 368) and ligand **6** with Mn plus methoxide and two molecules of methanol (*m*/*z*: 400). Thus, derivative **6** is complexed with Mn and methanol molecules replaced the acetate groups present in the starting manganese(II) acetate (**8**). A comparable result was obtained when ethanol + 0.1% of formic acid was used as solvent, with substitution of acetate groups by ethoxide groups.

In summary, the synthesis and structural analysis of three novel benzisothiazole-tetrazolyl derivatives (**4a**-**b** and **6**) from *pseudo*-saccharyl chloride **2** and tetrazoles **3a**-**b** and **5** were achieved. Complexation of compounds **4a** and **6** with manganese(II) acetate tetrahydrate complex, $Mn(CH_3COO)_2{\cdot}4H_2O$, lead to formation of two new benzisothiazole-tetrazolyl manganese complexes **7** and **8**.



Scheme 4.

At this stage, original strategies aiming at the coordination of transition metals (for instance: Ni, Co, Cu, Pd), with the three potential benzisothiazole-tetrazolyl nitrogen ligands synthesized, **4a**-**b** and **6**, are in progress. A subsequent investigation of catalytic applications of the resulting complexes (such as compounds **7** and **8**) was already devised and is the next step for this research.

4. Conclusions

Synthetic methodologies for the preparation of novel benzisothiazole-tetrazolyl derivatives, differing on the spacer-group used for linkage of the two heterocycles, were devised. Structural characterization of intermediate compounds through molecular orbital calculations (DFT(B3LYP)/6-31G(d,p)) was used to correlate structural features with differences in reactivity. The application of these compounds as nitrogen ligands for coordination with transition metals was also explored, leading to the easy preparation of *3-[1-(2-1H-tetrazol-5-yl)ethoxy]-1,2-benzisothiazole 1,1-dioxide-Mn(II) and N-(1,1-dioxo-1,2-benzisothiazol-3-yl)-amine-1H-tetrazole-Mn(II) complexes*.

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References

[1] M.L.S. Cristiano, R.A.W. Johnstone, P.J. Price, J. Chem. Soc., Perkin Trans. 1 (1996) 1453.
[2] A.F. Brigas, R.A.W. Johnstone, Tetrahedron Lett. 31 (1990) 5789.
[3] N.C.P. Araújo, A.F. Brigas, M.L.S. Cristiano, L.M.T. Frija, E.M.O. Guimarães, R.M.S. Loureiro, J. Mol. Catal. A: Chem. 215 (2004) 113.
[4] L.M.T. Frija, M.L.S. Cristiano, E.M.O. Guimarães, N.C. Martins, R.M.S. Loureiro, J. Bikley, J. Mol. Catal. A: Chem. 242 (2005) 241.
[5] J.A.C. Alves, J.V. Barkley, A.F. Brigas, R.A.W. Johnstone, J. Chem. Soc., Perkin Trans. 2 (1997) 669.
[6] M.L.S. Cristiano, R.A.W. Johnstone, J. Chem. Soc., Perkin Trans. 2 (1997) 489.
[7] M.L.S. Cristiano, R.A.W. Johnstone, J. Chem. Res. (1997) 164.
[8] J.V. Barkley, M.L.S. Cristiano, R.A.W. Johnstone, R.M.S. Loureiro, Acta Crystallogr. C: Cryst. Struct. Commun. 53 (1997) 383.
[9] M.L.S. Cristiano, A.F. Brigas, R.A.W. Johnstone, R.M.S. Loureiro, P.C.A. Pena, J. Chem. Res. (S) (1999) 704.
[10] N.C.P. Araújo, P.M.M. Barroca, J.F. Bickley, A.F. Brigas, M.L.S. Cristiano, R.A.W. Johnstone, R.M.S. Loureiro, P.C.A. Pena, J. Chem. Soc., Perkin Trans. 1 (2002) 1213.
[11] R. Almeida, A. Gómez-Zavaglia, A. Kaczor, M.L.S. Cristiano, M.E.S. Eusébio, T.M.R. Maria, R. Fausto, Tetrahedron 64 (2008) 3296.
[12] L.M.T. Frija, I.V. Khmelinskii, M.L.S. Cristiano, Tetrahedron Lett. 46 (2005) 6757.
[13] L.M.T. Frija, I.V. Khmelinskii, M.L.S. Cristiano, J. Org. Chem. 71 (2006) 3583.
[14] J.-M. Lehn, Supramolecular Chemistry, VCH, Weinheim, 1995.
[15] O. Kahn (Ed.), Magnetism: A Supramolecular Function, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1996.
[16] M.A.M. Abu-Youssef, F.A. Mautner, A.A. Massoud, L. Öhrström, Polyhedron 26 (2007) 1531.
[17] R.-G. Xiong, X. Xue, H. Zhao, X.-Z. You, B.F. Abrahams, Z.-L. Xue, Angew. Chem., Int. Ed. 41 (2002) 3800.
[18] Y.-J. Kim, Y.-S. Joo, J.-T. Han, S.H. Won, W.L. Soon, J. Chem. Soc., Dalton Trans. 18 (2002) 3611.
[19] A.K. Gupta, C.H. Song, C.H. Oh, Tetrahedron Lett. 45 (2004) 4113.
[20] A.S. Burukin, A.A. Vasilév, N.L. Merkulova, M.I. Struchkova, S.G. Zlotin, Russ. Chem. Bull., Int. Ed. 55 (2006) 118.
[21] P. Naumov, G. Jovanovski, Struct. Chem. 11 (2000) 19.
[22] F.A. Cotton, L.R. Falvello, W. Schwotzer, C.A. Murillo, G. Valle-Bourrouet, Inorg. Chim. Acta 190 (1991) 89.
[23] G. Jovanovski, B. Šoptrajanov, J. Mol. Struct. 174 (1998) 467.
[24] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03 (Revision C.02), Gaussian, Inc., Wallingford, CT, 2004.
[25] A.D. Becke, Phys. Rev. A 38 (1988) 3098.
[26] C.T. Lee, W.T. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[27] A.F. Brigas, C.S.C. Fonseca, R.A.W. Johnstone, J. Chem. Res. 6 (2002) 299.
[28] Z.P. Demko, K.B. Sharpless, J. Org. Chem. 66 (2001) 7945.
[29] Z.P. Demko, K.B. Sharpless, Org. Lett. 3 (2001) 4091.
[30] B.D. Song, W.P. Jenks, J. Am. Chem. Soc. 111 (1989) 8470.
[31] M. Muttenthaler, M. Bertel, P. Weinberger, G. Hilscher, W. Linert, J. Mol. Struct. 741 (2005) 159.