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Review

Fascinating variability in the chemistry and properties of 2,6-bis-(benzimidazol-2-yl)-pyridine and 2,6-bis-(benzthiazol-2-yl)-pyridine and their complexes

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Spectra

ABSTRACT

A review of papers up to 2008 dealing with all branches of chemistry of the compounds containing 2,2′-pyridine-2,6-diylbis(1H-benzimidazole) and 2,2′-pyridine-2,6-diylbis(1,3-benzothiazole) is presented. The review summarizes the preparation procedures and properties of free organic compounds, as well as their different protonated and/or deprotonated forms. A summary of complex compounds of the considered ligands is presented together with the review of the most important properties such as spectroscopic properties, structures, magnetic properties or biological and electrochemical activity. From this review the blind spots can be identified which might suggest more points of potential interest. Also missing is a promising investigation of, at present unknown, analogues.

1. Introduction

There is a plethora of literature data referring to compounds containing aromatic rings such as pyridine, imidazole, benzimidazole, etc. and many review articles on them are available e.g. [1–17]. However, no review deals with compounds containing 2,6-bis-(benzimidazol-2-yl)-pyridine (*bzimpy*) and 2,6-bis-(benzthiazol-2-yl)-pyridine (*bztpy*). There are several motivations for studying such compounds and their complexes as follows.

(a) These molecules or their derivatives usually function as tridentate ligands but sometimes they provide wider possibilities of coordination (e.g. formation of helical structures or bridging through the nitrogen atom of the pyridine ring or lower functionality) [18–27].
(b) The same ligand with the same central atom can aggregate in different metal to ligand molar ratio, such as 1:1 or 1:2 depending on the counter-anion involved [28].
(c) Some complexes of these ligands exhibit spin crossover behaviour in the solid state as well as in solution [29–33].
(d) The versatility of these ligands allows one to study the manifold factors that influence the spin crossover behaviour; an involvement of these ligands into the hydrogen bond network and a possibility of their deprotonation results in the redistribution of the electron density [34].
(e) The substitution of the N–H bond at the benzimidazole ring for the N–R group allows one to study the importance of the hydrogen bond network.
(f) A possibility of forming the 4-substituted derivatives could enrich the coordination chemistry as a whole [33,35] or significant changes in selected properties can be reached [33,35–38].
(g) The literature data about the magnetic and other properties of the complexes of these ligands are incomplete and often controversial, so that there is a need of their further revision e.g. [33] *vs.* [36,36] *vs.* [39,40] *vs.* [41] or [42] *vs.* [43].
(h) Properties of the complexes with the ligands *bzimpy* and *bztpy* can be compared with the data for complexes with the ligands substituted in the 4-position.
(i) These ligands also provide many interdisciplinary links to biochemistry (interaction with biomolecules [44]), electrochemistry (utilization in photoelectrochemical solar cells [45,46]), car industry, catalytic properties [47–49], chemistry of polymers [50], or separation of lanthanides and actinides [51], etc.

This review is focused on the compounds (free ligands and their complexes) containing unsubstituted *bzimpy* and *bztpy* with the exception of their protonated and/or deprotonated forms.

The following text contains detailed description of the free ligands – their preparation, characterization and structure and acid-base properties. Then a description of complex compounds of these ligands follows, completed with some summarizing tables. At the end a short comparison of characteristic items of the compounds is presented.

2. Free ligands

A significant source of confusion in the literature is the different notation of the title compounds. According to IUPAC rules the correct notations for 2,6-bis-(benzimidazol-2-yl)-pyridine is 2,2′-pyridine-2,6-diylbis(1H-benzimidazole) (Table 1) and for 2,6-bis-(benzthiazol-2-yl)-pyridine the correct notation is 2,2′-pyridine-2,6-diylbis(1,3-benzothiazole). However, majority of the authors use the non-IUPAC notations that even differ from each other. They are summarized in Table A1 in Appendix A. Here, we will keep to the most frequently used notation, i.e. 2,6-bis-(benzimidazol-2-yl)-pyridine.

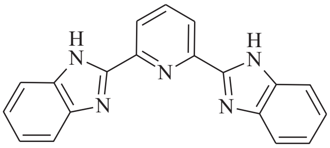
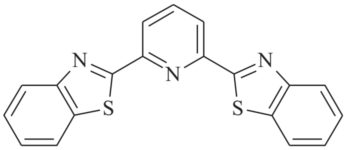
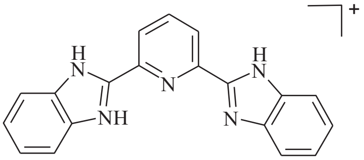
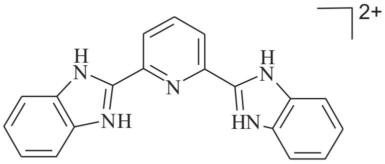
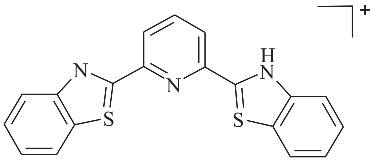
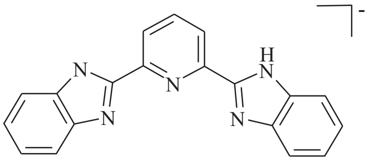
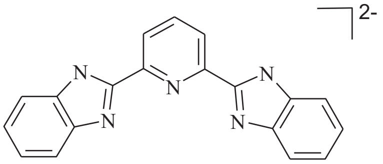
The additional source of confusion could be the abbreviations of the ligands as there is no uniform recipe accepted in the literature for their notation. The most frequently used abbreviation is *bzimpy* for the electroneutral molecule of 2,6-bis-(benzimidazol-2-yl)-pyridine. However, some authors use also abbreviation H_2*bzimpy* (2,6-bis-(1H-benzimidazol-2-yl)-pyridine) for the free neutral ligand as well as many others. All of the abbreviations are summarized in Table A1 in Appendix A together with different notations. The notation H_2*bzimpy* has the advantage that it emphasizes the presence of acidic hydrogen atoms. We will generally employ the abbreviation *bzimpy* since usually the presence of the acidic hydrogen atoms is not emphasized (see Table A1 in Appendix A). Table A2 in Appendix A summarizes non-IUPAC notation and different abbreviations for benzthiazole analogue. The situation is even more complicated by the fact that different notation is often used in a single paper for the same ligands e.g. [27].

The ligand 2,6-bis-(benzimidazol-2-yl)-pyridine can be protonated or deprotonated. Consequently, a wide series of different notation was introduced. The IUPAC names of both the protonated and deprotonated ligand 2,6-bis-(benzimidazol-2-yl)-pyridine are summarized in Table 1 and non IUPAC names together with different abbreviations are summarized in Table A1 in Appendix A.

2.1. 2,6-Bis-(benzimidazol-2-yl)-pyridine

In general, the majority of benzimidazole derivatives together with 2,6-bis-(benzimidazol-2-yl)-pyridine can be prepared by

Table 1
Free ligands under study.

Abbreviation	Formula	IUPAC names [52]
bzimpy		2,2′-Pyridine-2,6-diylbis(1H-benzimidazole)
bztpy		2,2′-Pyridine-2,6-diylbis(1,3-benzothiazole)
(*Hbzimpy*)$^+$		2-[6-(1H-benzimidazol-2-yl)pyridin-2-yl]-1H-3,1-benzimidazol-3-ium
(*H$_2$bzimpy*)$^{2+}$		2-[6-(1H-benzimidazol-3-ium-2-yl)pyridin-2-yl]-1H-3,1-benzimidazol-3-ium
(*Hbztpy*)$^+$		2-[6-(1,3-Benzothiazol-2-yl)pyridin-2-yl]-1,3-benzothiazol-3-ium
(*bzimpy*$_{-H}$)$^-$		2-[6-(1H-benzimidazol-2-yl)pyridin-2-yl]benzimidazol-1-ide
(*bzimpy*$_{-2H}$)$^{2-}$		2,2′-Pyridine-2,6-diylbis(benzimidazol-1-ide)

a one-step condensation reaction of the carboxylic acid (2,6-pyridinedicarboxylic acid) with a diamine (1,2-diaminobenzene) in syrupy phosphoric acid at ca. 200 °C (Fig. 1).

The final product, after recrystallization, can be solvated owing to the hydrogen bonds [53]. The mechanism probably involves a Schiff condensation in the first stage, the cyclization yielding the imidazolidine rings, and finally oxidation by air – this condition producing the aromatic imidazole ring (see later for *bztpy*).

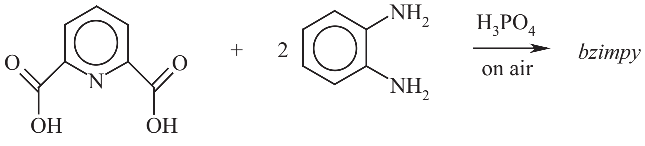
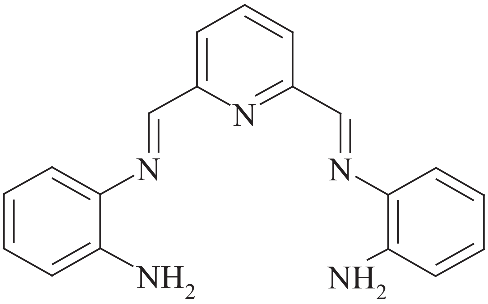


Fig. 1. Preparation of *bzimpy*.

The ligand *bzimpy* was also prepared by template synthesis when a lanthanide salt reacts with the 1,2-diaminobenzene and 2,6-pyridinedicarboxaldehyde [54]. In addition to the macrocyclic Schiff base-complex (L^1) (Fig. 2), the *bzimpy*-complex was also formed.

A template synthesis of 2,6-pyridinedicarboxaldehyde with 1,2-diaminobenzene and Cd(ClO$_4$)$_2$ gave the Schiff base-complex (CdL^1((ClO$_4$)$_2$ [55]. When this complex reacted with Ni(ClO$_4$)$_2$ under aerobic conditions a Ni(II) complex with *bzimpy* was isolated in two days. Under anaerobic conditions the formation of *bzimpy* does not proceed. The mechanism is visualized in Fig. 3. It involves an intramolecular nucleophilic addition of the nitrogen atom of NH$_2$ group to the electrophilic C-centre of the C=N Schiff base, and then a cyclization followed by oxidation. The formation of the ligand *bzimpy* from L^1 was also observed upon application of different experimental conditions: (i) spontaneous oxidation of a solution of ligand L^1 in weakly acidic media [54], (ii) interaction of



L^1

Fig. 2. A macrocyclic Schiff base L^1.

the ligand L^1 in $CHCl_3$ in air with silica gel [56], (iii) interaction of the ligand L^1 in MeOH with I_2 [56], (iv) reaction of L^1 with $Cu(OAc)_2$ in MeCN–MeOH mixture [56].

The ligand *bzimpy* can also be synthesized using microwave irradiation [57].

Free *bzimpy* can exist in three geometrical isomeric forms. The position of the amine and imine nitrogen atoms can be depicted as *cis*-N_{bzim}-N_{py}-N_{bzim}, *cis*-N_{bzim}H-N_{py}-N_{bzim}, and *cis*-N_{bzim}H-N_{py}-N_{bzim}H configuration or, if we consider the imine nitrogen atoms relative to the pyridine nitrogen atoms, we can speak about *cis–cis*, *trans–cis* or *trans–trans* configuration (Fig. 4).

The presence of individual isomers can be monitored by NMR spectroscopy. The NMR spectra of the free *bzimpy* were taken several times [23,34,58]. In the first study in DMSO-d_6, a rapid NH imino-protons exchange with water protons was observed [58]. Assignment of the ^{1}H and ^{13}C signals was done and this was reproduced in later work [23,34].

The neutral molecule, as well as protonated/deprotonated *bzimpy*, was studied in THF-d_8 and DMSO-d_6 solvents [34]. The neutral ligand adopts the *cis*-N_{bzim}H-N_{py}-N_{bzim}H conformation at $-90\,^{\circ}$C as well as at room temperature. This conformation is stabilized by hydrogen contacts which conclusion is supported by calculations (Fig. 5). The formation of the *cis*-N_{bzim}H-N_{py}-N_{bzim}H conformation but in asymmetric arrangement due to a hydrogen bond on only one side was monitored based on NMR and IR spectroscopy [59]. The above configuration is also found in (CD_3)CO [24] but this observation is contradicted in another report [60].

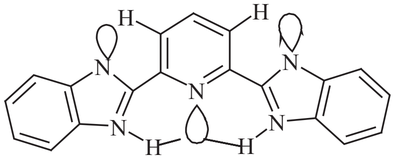


Fig. 5. Stabilization of the *bzimpy* by hydrogen contacts in *cis*-N_{bzim}H-N_{py}-N_{bzim}H conformation.

The ^{1}H, ^{13}C and DIFNOE-NMR spectra in d_6-acetone indicate a considerably different situation. The acidic hydrogen probably dissociates and migrates between both nitrogen atoms. For this reason it cannot be differentiated between the amine and imine nitrogen atoms; both atoms seem to be equivalent. Consequently, a differentiation among conformers loses meaning. However, the DIFNOE experiment indicates that hydrogen atoms H2 and H11 interact through space. Thus the existence of the conformer *cis–cis* is preferred and has a higher statistical weight than the *trans–cis* or *trans–trans* conformers. The fast migration could be suppressed, partially or completely, at low temperature. In the solid state, hydrogen migration is not permitted so that to speak about conformers sounds more reasonable [60].

MO calculations showed that *bzimpy* forms a partially planar structure consisting of a pyridine ring and one benzimidazole group whilst the other imidazole group may be twisted around the C–C single bond in alcoholic solvents [61].

Two phases of the free ligand were obtained with different water content [62]. The first phase is a monohydrate *bzimpy*·H_2O containing one ligand molecule and one water molecule in each asymmetric unit. Sesquihydrate *bzimpy*·1.5H_2O contains two ligand molecules and three water molecules in the asymmetric unit. Both compounds crystallize in $P2_1/c$ space group and in both cases a hydrogen bond network is formed. The geometry of the ligand molecules is similar but their packing is considerably different as a consequence of the different hydrogen-bonding scheme. This is related to the main difference in the molecular geometries that arise from the different rotation of the lateral wings around C–C single bonds. However, in both cases the *cis*-N_{bzim}H-N_{py}-N_{bzim}H configuration occurs. Another solvated structure of the free ligand

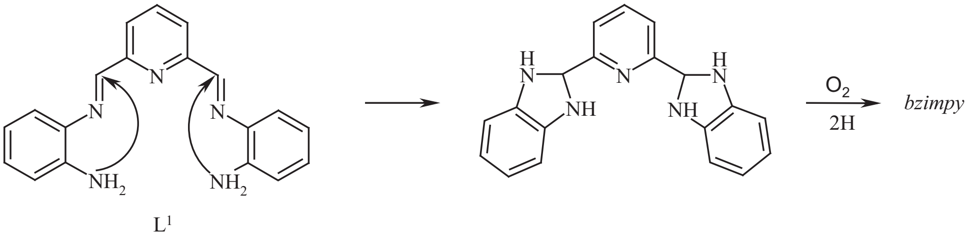
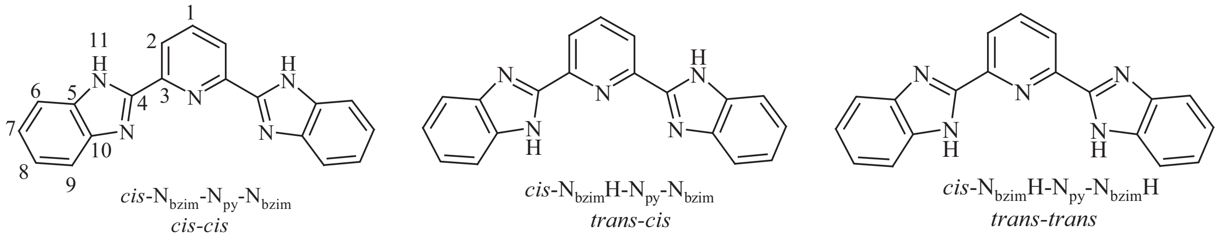


Fig. 3. Cyclization of Schiff base L^1 to *bzimpy* on air conditions.



cis-N_{bzim}-N_{py}-N_{bzim}
cis-cis

cis-N_{bzim}H-N_{py}-N_{bzim}
trans-cis

cis-N_{bzim}H-N_{py}-N_{bzim}H
trans-trans

Fig. 4. Different configurations of the ligand *bzimpy*.

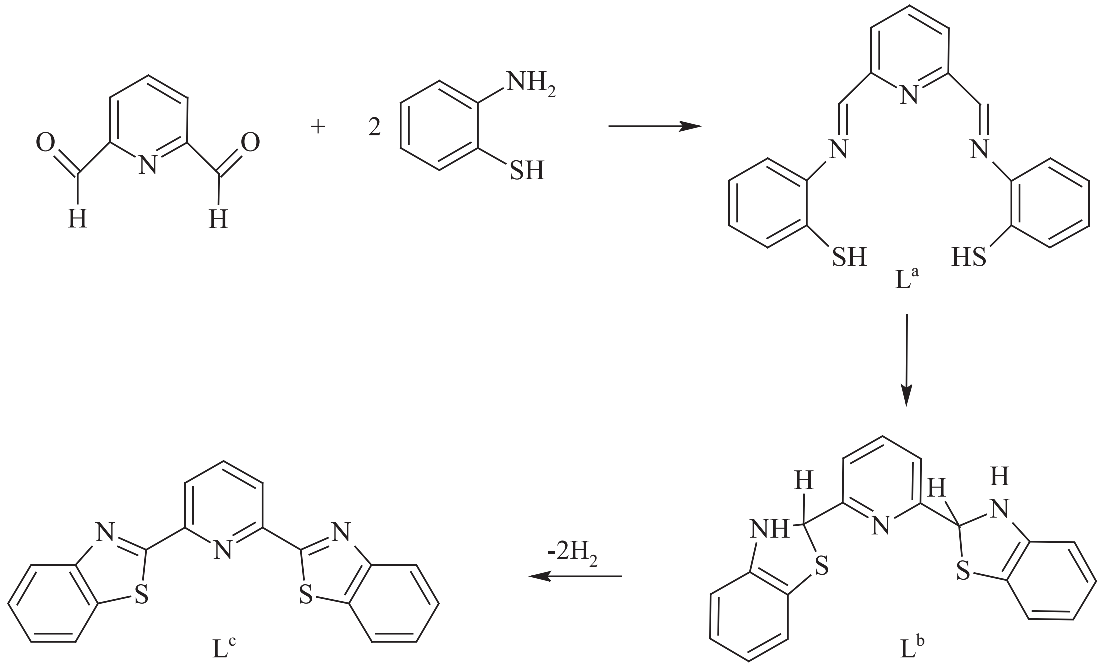


Fig. 6. The formation scheme of 2,6-bis-(benzthiazol-2-yl-)pyridine.

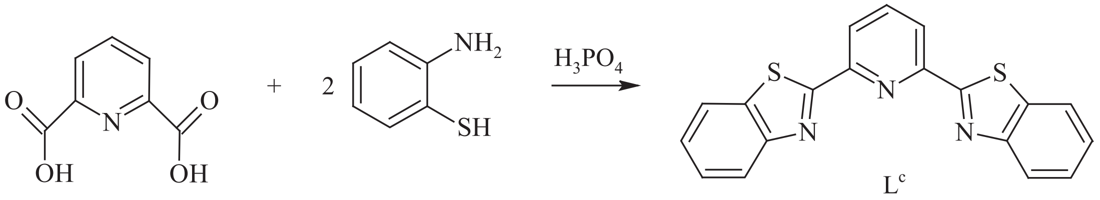


Fig. 7. Preparation of 2,6-bis(benzthiazol-2-yl)pyridine in phosphoric acid.

with different cell parameters is *bzimpy*·EtOH ($P2_1/c$ space group) [63].

The uncoordinated ligand was detected in the hydroxotriphenyltin compound $[Sn(C_6H_5)_3(OH)]$·*bzimpy*·H_2O [64]. In this structure, the water molecule possesses a hydrogen contact through both acidic hydrogen atoms of the ligand of the *cis*-N_{bzim}H-N_{py}-N_{bzim}H configuration. Additional hydrogen contacts give rise to a two-dimensional network structure.

Bzimpy, as a free organic compound was investigated as receptor for binding urea with high affinity. The structure of the complex between *bzimpy* and urea in the ratio 1:1 and 2:1 was determined [65]. The urea molecule fits into the cavity of *bzimpy* and is bound to the NH protons and the carbonyl oxygen of urea is pointed inwards into the cavity of the receptor. It seems that the configuration with imine hydrogen oriented inside the cavity is preferred in any structures that consist of the *bzimpy* ligand and non-metal fragment.

In all *bzimpy* complexes known so far the configuration *cis*–*cis* was observed. The structure of the N-methyl substituted ligand in the protonated form is also known [66].

Electro-polymerization of *bzimpy* was studied giving electroactive conducting polymers with potential as an electrocatalyst for reduction of O_2, CO_2 and H^+ [48].

2.2. 2,6-Bis-(benzthiazol-2-yl)-pyridine

The condensation of the aldehyde or ketone with primary aliphatic or aromatic amine in methanolic solution usually provides a Schiff base. Thus one could expect the formation of the Schiff base L^a as a product of the condensation of the 2,6-pyridinedicarboxaldehyde with 2-aminothiophenole. In fact its isomer L^b is formed. This isomer is unstable and is oxidized forming the final product L^c 2,6-bis-(benzthiazol-2-yl)-pyridine (Fig. 6) [67].

A similar scheme is also valid for the benzoxazoline analogue.

The ligand 2,6-bis(benzthiazol-2-yl)pyridine can also be prepared by condensation of the 2,6-pyridindicarboxylic acid with 2-aminothiophenole in syrupy phosphoric acid at 120–220 °C (Fig. 7) [68].

As mentioned above, the condensation of 2-aminothiophenol with aldehyde does not lead to the formation of the corresponding Schiff base but the formation of benzthiazolines or their oxidation products; benzthiazoles are preferentially formed. The Schiff base can be prepared by complexation of methylated benzthiazoline with zinc or cadmium acetate [69] or thallium acetate [70]. The non-substituted benzthiazoline product with zinc acetate gives rise to a hydrogenation–dehydrogenation reaction, in which one ring is aromatised and the second one takes up the hydrogen atom split from the first one. In the next step the protonated ring is opened and deprotonated (Fig. 8) [71]. Benzthiazolines can also isomerize to Schiff bases in a basic environment [72].

A free ligand *bztpy* could also exist in three isomeric forms because of rotation of the benzthiazole groups. In these isomers the position of the nitrogen and sulfur atoms can be depicted as *cis*-N_{bzt}-N_{py}-N_{bzt}, *cis*-S_{bzt}-N_{py}-N_{bzt} and *cis*-S_{bzt}-N_{py}-S_{bzt} configuration or if we consider imine nitrogen atoms relatively to pyridine nitrogen atoms we can speak about *cis*–*cis*, *trans*–*cis* or *trans*–*trans* configuration (Fig. 9).

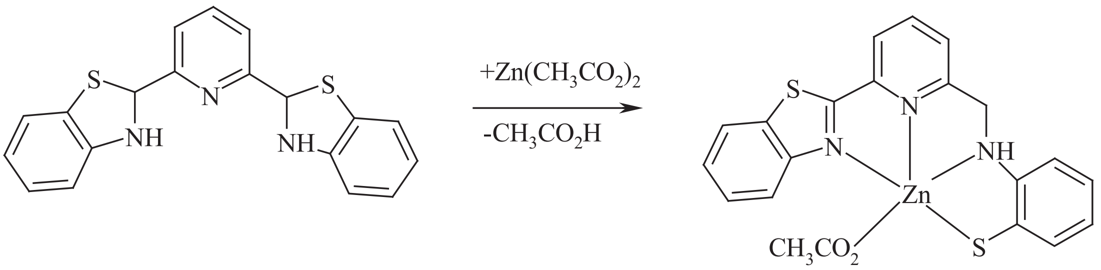


Fig. 8. Hydrogenation–dehydrogenation reaction of the benzthiazoline product.

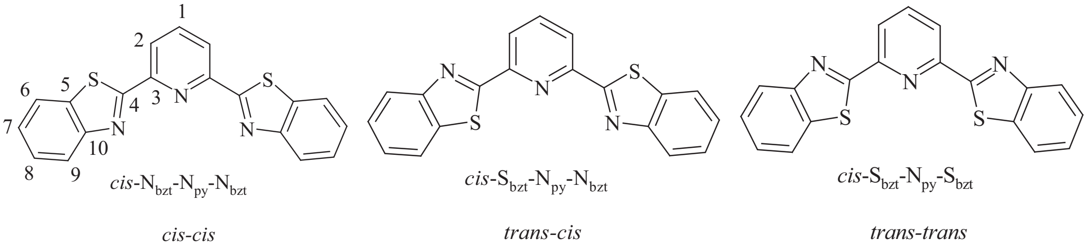


Fig. 9. Different configuration of the ligand *bztpy*.

Semiempirical MO calculations (using AM1 method of the Hyperchem package [73]) indicate that the energy differences between these isomers are small; the minimum energy, however, adopts the *trans*–*trans* isomer [28].

The experimental evidence for the presence of a certain conformer is provided by NMR spectroscopy. The ^{1}H, ^{13}C and CH-COSY spectra in $CDCl_3$ exclude the existence of the *trans*–*cis* isomer because of high symmetry of the spectra. It was not possible to distinguish between *cis*–*cis* and *trans*–*trans* isomers from NMR spectra, but the existence of only one isomer in solution can be predicted: either *cis*–*cis* and *trans*–*trans* [28]. In order to confirm this statement some more experiments need to be done at lower temperatures.

The structure of the *bztpy* of good quality is not available, but the unambiguous structural motif can be seen from the preliminary solution of the structure with the *trans*–*trans* configuration [28]. It seems that the free molecule is slightly distorted from planarity with the angle between pyridine and benzthiazole rings being 7.38°.

2.3. Protonated/and deprotonated forms of the 2,6-bis-(benzimidazol-2-yl)-pyridine and 2,6-bis-(benzthiazol-2-yl)-pyridine

The ligand *bzimpy* reacts with aqueous hydrohalic and perchloric acids to provide adducts of the formula *bzimpy·HX* (X = Cl, Br, I and ClO_4) [40].

In order to distinguish between protonated and deprotonated forms it is reasonable to label protonated ligands as $H_a bzimpyX$ where *a* represents number of acidic hydrogen atoms and *X* is the anion of the corresponding acid. The deprotonated ligand then can be labelled $Mbzimpy_{-bH}$ where *b* represents the number of released hydrogen atoms and *M* is the counter-cation (compare with Tables 1 and A1 and corresponding text).

By the reaction of the *bzimpy* with trichloracetic acid the doubly protonated molecule $(H_2bzimpy)^{2+}$ can be obtained with some portion of pyridinic protonation as well. Usage of a stronger acid such as H_2SO_4 provides a fully protonated compound $(H_3bzimpy)^{3+}$ [34]. Compounds $Na_2(bzimpy_{-2H})$ and $Li_2(bzimpy_{-2H})$ containing deprotonated ligand *bzimpy* for NMR investigation were also prepared [34].

The structures of protonated $(Hbzimpy)(ClO_4)\cdot H_2O$ [74] and $(Hbztpy)(ClO_4)\cdot H_2O$ [28] were described. Cell parameters for $(Hbzimpy)(ClO_4)\cdot H_2O$ clearly define the monoclinic ($P2(1)/n$) crystal system. Structural analysis revealed that the ligand in the solid state is either in the protonated *cis*-N_{bzim}H-N_{py}-N_{bzim}H configuration or that of the protonated *cis*-N_{bzim}H-N_{py}-N_{bzim} configuration. The latter one is, however, less probable. An extended hydrogen bonding network was identified in the system (Fig. 10).

Cell parameters of protonated $(Hbztpy)(ClO_4)\cdot H_2O$ define a monoclinic ($P2(1)/n$) crystal system. In addition, the *trans*–*trans* conformation as in the free *bztpy* was observed.

The structures of the protonated forms of the ligands *bztpy* and *bzimpy* show some similarity. Both systems crystallize in the monoclinic system, in the same space group with very similar cell parameters. The positions of the imine nitrogen atoms are *trans*-relative to the pyridine nitrogen atom; protonation of the pyridine nitrogen atom can be excluded. Both structures contain cations of the ligand, perchlorate anions and one water molecule. Arrangement of the cations forms a system of puckered layers.

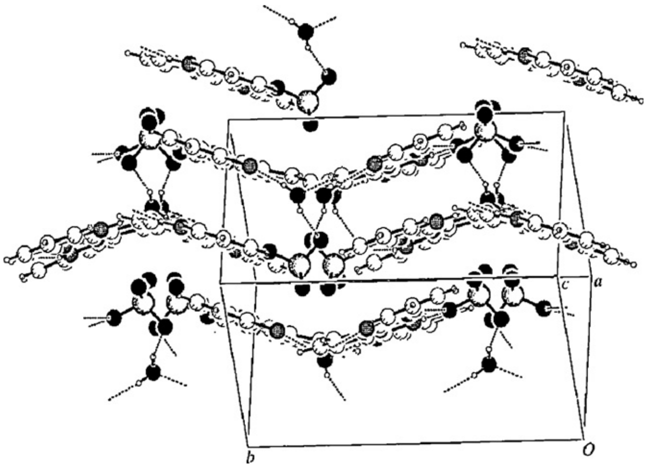


Fig. 10. A packing diagram illustrating the hydrogen-bonding network in $(Hbzimpy)(ClO_4)\cdot H_2O$ and the system of puckered layers. According to [74] with kind permission from the publisher.

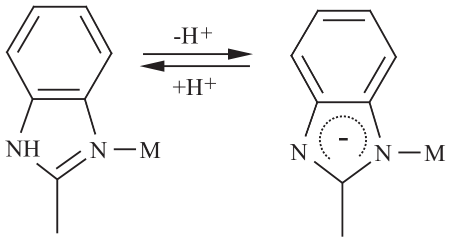


Fig. 11. Dissociation equilibrium of the acid proton.

3. Structure and properties of complexes

A relatively wide range of data is available in the literature concerning the preparation, characterization and application of complexes with *bzimpy* and *bztpy*. Many compounds have been characterized by classical methods such as IR, UV/vis or magnetic properties, etc., however often without appropriate discussion. Some special characterization tools have been applied as well, e.g. Evans NMR method [75] for investigation of magnetic properties of the complexes in solution or different bio-applications have been described.

It is supposed that the complexes with *bztpy* will be less stable than terpyridine complexes because the nitrogen atoms in the five-member heterocycles have weaker donor properties than the pyridine nitrogen atoms. This arises from the fact that benzthiazole ($pK_a = 1.2$) [76] is a much weaker base than pyridine ($pK_a = 5.2$) [77]. The pK_a value for benzthiazole is 1.41 [78]. Moreover, it can be supposed that complexes with 2,6-bis-(benzimidazol-2-yl)-pyridine will be the most stable, because benzimidazole is the strongest base ($pK_a = 5.53$ [79]) in the series. Some authors suppose a preferable coordination of the pyridine nitrogen atom relative to the imidazole nitrogen atom [40]. However, this has no support from quantum-chemical calculations [33]. A comparison of the acidic pK_as of coordinated *bzimpy vs.* the free ligand is given below for some ruthenium complexes (see Section 3.1 d^6 systems).

The type of donor atom has a strong effect on the ligand field strength in the series of the ligands 2,6-bis-(benzthiazol-2-yl)-pyridine, 2,6-bis-(benzoxazol-2-yl)-pyridine and 2,6-bis-(benzimidazol-2-yl)-pyridine. This effect can be reflected in different magnetic properties of the complexes. In general, Fe(II) complexes of *bzimpy* and *bztpy* may show spin crossover whilst complexes with 2,6-bis-(benzoxazol-2-yl)-pyridine prefer the high spin state over the studied temperature range [80]. This statement has exceptions as will be shown later.

The benzimidazole group is a stronger σ-electron donor relative to the pyridile or pyrazole groups. Moreover, one may suppose an easier dissociation of the imidazole hydrogen atom after coordination of the ligand to the central atom. Thus, physico-chemical properties of the complexes could be controlled by driven or spontaneous dissociation equilibrium of the acid proton (Fig. 11) [58]. Also some examples were encountered where the ligands were protonated but the final compound was not a complex but merely a ligand with some counter anion.

Since strong solvation is expected for the pure ligand *bzimpy* as a result of its strong affinity for hydrogen bonding [53], strong solvation can also be expected in its complexes. This solvation can be even stronger in complexes, partly because other fragments such as counter anions are present in the structures.

The ligand *bzimpy* has the ability to bind halide anions [81], showing high selectivity for fluoride over other halide anions. The binding of the ligand with a series of anions was monitored by changes in ^1H NMR chemical shifts, as well as by UV–visible and fluorescence spectroscopy. The ligand seems to be the simplest tridentate molecule used for anion recognition that shows high binding constants. This enables the use of this ligand as a sensor for the detection of fluoride ions. A complete survey of the complexes with the ligand *bzimpy* is in Table A3 in Appendix B.

3.1. *Complexes of the ligand 2,6-bis-(benzimidazol-2-yl)-pyridine*

3.1.1. *d^0-system–Zr(IV), V(V), Mo(VI), W(VI)*

The zirconium complex with a two times deprotonated ligand $[Zr(bzimpy_{-2H})Cl_2]$ is an active catalyst for the polymerization of methyl acrylate via coordination polymerization in the presence of methylaluminoxane. The dominant mechanism for methyl acrylate polymerization is the metal-methylaluminoxane coordination polymerization. Methyl acrylate polymerization by methylaluminoxane alone and by just thermal heating is negligible [47].

The vanadium(V) complex $[VO_2(bzimpy_{-H})]\cdot 1.25H_2O$ provides the complex with a singly deprotonated ligand whilst vanadium(IV) provides a complex with an electro-neutral ligand [82].

Peroxo complexes $[\{MoO(O_2)_2\}_3(bzimpy)_2]$ and $[\{WO(O_2)_2\}_3(bzimpy)_2]$ are thought to be trinuclear, each having a pentagonal bipyramidal structure with two different environments around the central atoms [83]. This is supported by the continuous loss of peroxo groups upon heating. However, in the case of the trinuclear complex the ligand should be in the *cis*-N_{bzim}H-N_{py}-N_{bzim} configuration (in all other complexes the *cis*-N_{bzim}-N_{py}-N_{bzim} configuration was observed).

3.1.2. *d^1 systems – V(IV)*

In vanadium(IV) complex $[VO(bzimpy)(H_2O)_2](CF_3SO_3)_2\cdot 2H_2O$, based on EPR, tautomerism V=O *vs.* V-OH_2 was suggested in DMF solution [82]. In the structure, three coordination positions are occupied by nitrogen atoms of the ligand and the remaining coordination positions are occupied by two water oxygen atoms (in *trans* position) and by one oxygen atom of an oxo-group.

3.1.3. *d^3 systems – Cr(III), Re(V)*

Coordination of the chloride atoms in the complex $[Cr(bzimpy)Cl_3]$ was proved by IR spectra [84]. The magnetic moment at room temperature is 3.8 B.M.

In the $[Cr(bzimpy)_2]Cl$ complex the starting ligand and coordinated one was the same *bzimpy* = 2,6-bis-(benzimidazol-2-yl)-pyridine. This seems to be misleading because after coordination each ligand is deprotonated and thus $bzimpy_{-H}$ and the complex should be written as $[Cr(bzimpy_{-H})_2]Cl$. (Probably one more mistake was introduced when the authors stated that the ESI mass spectrum base peak at $m/z = 627$ was due to $[Cr(bzimpy)]^+$ instead of to $[Cr(bzimpy_{-H})_2]^+$.) They concluded that the complex binds to DNA with moderate strength and that the complex interacts with the DNA surface [85].

X-ray investigation of the oxo-bridged binuclear complex $[(\mu\text{-}O)\{ReOCl_2(bzimpy_{-H})\}_2]\cdot 2H_2O\cdot 2DMF$ [86] revealed that the ligand *bzimpy* coordinates as a tridentate monoanionic chelate with deprotonation of one imidazole nitrogen. As the source of the bridging oxo group, atmospheric water was identified. Each rhenium atom is coordinated in the equatorial plane by an N_3Cl donor set and the axial positions are occupied by two different types of oxygen atoms, a terminal one and a bridging one, respectively. An extended hydrogen bonding network was identified, involving the lone pair of electrons on the deprotonated imino group.

3.1.4. *d^5 systems – Mn(0), Mn(II), Fe(III), Ru(III)*

In the dinitrosylmanganese complex $[Mn(NO)_2(CN)_2(bzimpy)]\cdot H_2O$ [87] manganese(0) has a low-spin $\{Mn(NO)_2\}^7$ electron configuration (in respect to the notation by [88]). Based on two ν(NO) modes and only one ν(CN) mode, it is reasonable to propose monomeric structures of the complex.

Moreover, the ligand *bzimpy* was suggested to behave as a tridentate one, resulting in the sevenfold coordination of the central manganese atom.

The manganese complexes can serve as biological models [89]. With Mn(II) the following complexes M:L = 1:1 and 1:2 were prepared: (Mn(bzimpy)Cl_2(, (Mn(bzimpy)Cl_2(·DMF, (Mn(bzimpy)$(Ac)_2$(, (Mn$(bzimpy)_2(SO_4)$(·$4H_2O$, [Mn$(bzimpy)_2$]$(NO_3)_2$·$3H_2O$, (Mn$(bzimpy)_2$(($ClO_4)_2$·$3H_2O$ [90]. Based on IR and UV/vis spectra, electrical conductivity and thermal analysis, the complex (Mn$(bzimpy)_2(SO_4)$(·$4H_2O$ is probably six-coordinated from the coordination point of view; it means that one ligand is tridentate, the second ligand is only bidentate, and the sulfate group is monodentate. On the basis of IR spectra the monodentate coordination of an acetyl group is expected whilst perchlorate and nitrate groups are uncoordinated. The structure of the (Mn(bzimpy)Cl_2(·DMF complex is described as a distorted square pyramid with three nitrogen atoms and one chloro ligand forming the base. The axial position is occupied by the second chloro ligand [90]. The complex [Mn$(bzimpy)_2$]$(ClO_4)_2$ was characterized only by IR and UV/vis spectra [36].

The [Mn$(bzimpy)_2$]$(ClO_4)_2$ complex is believed to be six coordinate and the [Mn(bzimpy)Cl_2]·0.5MeOH complex is five coordinate. A detailed comparison of a set of magneto-chemical parameters values from susceptibility measurement and EPR, including zero-field splitting, obtained by both techniques (using EPR, also solid and frozen liquid data) was given [91]. Both complexes were HS with effective magnetic moments close to spin-only value. Also some *ab initio* calculations were carried out. From optimization of the geometries of [Mn$(bzimpy)_2$]$^{2+}$ and [Mn(bzimpy)Cl_2] bond distances were obtained. The ligand *bzimpy* in [Mn(bzimpy)Cl_2] is bonded weaker than in [Mn$(bzimpy)_2$]$^{2+}$. Calculated bond distances in [Mn(bzimpy)Cl_2] are very close to those obtained by experiment on (Mn(bzimpy)Cl_2(·DMF [90]. In both complexes only slight zero-field splitting was identified. However, the match between AC susceptibility and EPR magnetic parameters was not perfect.

The complex [Mn(bzimpy)Cl_2]·0.5MeOH has only moderate ZFS [92,93] with the following magnetic data $g_x = 2.057$, $g_y = 1.880$, $g_z = 1.944$, $D/hc = -2.74\,cm^{-1}$, $E/hc = 2.23\,cm^{-1}$, and $zJ/hc = 0.385\,cm^{-1}$ that slightly differs from those given in [94].

In the structure of the [Mn$(bzimpy_{-H})_2$] complex, prepared from Mn$(OOCMe)_2$ in absolute ethanol (in the original paper the deprotonated ligand is labelled as *bzimpy*) [95], two coordinated ligands *bzimpy* give distorted octahedral coordination of the central atom. The system of hydrogen bonds was also identified. The cyclic voltametric measurements revealed that the complex is capable of reconstituting the water-oxidizing complex of photosystem II in plant photosynthesis with great efficiency. The same complex was used also for the study of photoactivation of Mn-depleted photosystem II [96].

With the aim of investigating potential superoxide dismutase mimicry on Mn(II) compounds the complex [Mn$(bzimpy_{-H})_2$]·ethylacetate·H_2O was prepared from the chloro-complex precursor that was refluxed in methanol followed by recrystallization from a mixture of DMSO:etylacetate:water 1:1:0.5 [97]. It is interesting that the deprotonated form of the ligand was stabilized without addition of any base. The coordination geometry shows considerable distortion from a regular octahedron. In this case the difference between bond lengths of Mn-N_{py} and Mn-N_{bzim} is not as significant as in the case of other central atoms (Fe, Ni, Ru. . .). Moreover, one Mn-N_{py} bond is longer than one Mn-N_{bzim} bond. The complex is in HS state. From the EPR in DMSO at 77 K it is clear that complex adopts a monomeric structure in this solvent [97].

Based on the EPR spectra of the complex [Fe(bzimpy)Cl_3], its state was described as high spin at 77 K, whilst for the complex [Fe$(bzimpy_{-2H})_2$][$NHEt_3$]·$4H_2O$ the low spin state was indicated (with traces of iron(III) HS) [29]. The complex [Fe(bzimpy)Cl_3] was studied as functional models for the intradiol-cleaving catechol dioxygenase enzymes [98]. On replacing the bulky benzimidazole groups by the carboxylate groups, the yield of the intradiol cleavage products of dioxygenation increased.

For the complex [Fe$(bzimpy)_2$]$(ClO_4)_3$ [99] EPR spectra provided the following values: $g_\perp = 2.237$ and $g_{||} = 1.923$ for the powder and $g_\perp = 2.242$ and $g_{||} = 1.915$ for the solution (methanol:DMF = 3:1) at 100 K. The axial symmetry of the spectrum is in accordance with the expected symmetry of the complex. A $^2B_2$ ground state (in D_{4h}) was suggested (in powder).

The complexes of Fe(III), [Fe$(bzimpy)_3$]$(ClO_4)_3$·S (S = $2H_2O$, $2H_2O$·2EtOH) or Fe$(bzimpy)_2(BF_4)_3$·0.5EtOH, can also be formed. It is expected that one ligand molecule in the complex containing three molecules of the ligand *bzimpy* is not coordinated and is stacked in the structure by hydrogen bonding [60]. The complex Fe$(bzimpy)_3(ClO_4)_3$·$2H_2O$ is in low spin state.

A series of ruthenium(III) complexes was synthesized with the following composition [Ru(bzimpy)Cl_3], [Ru$(bzimpy_{-H})$(bpy)Cl][PF_6], Ru$(bzimpy_{-H})$(bpy)(NO_3)][PF_6], Ru$(bzimpy_{-H})(bpy)_2$][$(PF_6)_2$], Ru$(bzimpy_{-H})$(phen)Cl][PF_6] and Ru$(bzimpy_{-H})(phen)_2$][$(PF_6)_2$] (bpy = 2,2′-bipyridine, phen = 1,10-phenantroline) [100]. These complexes display expected IR, ^{1}H NMR, UV/vis and EPR characteristics. In the two complexes Ru$(bzimpy_{-H})(bpy)_2$][$(PF_6)_2$] and Ru$(bzimpy_{-H})(phen)_2$][$(PF_6)_2$] the number of nitrogen atoms with potential to coordinate to the central atom is 7. The ligand *bzimpy* coordinates only through two donor atoms, one benzimidazole and one pyridine nitrogen atom. Ruthenium binuclear complexes with mixed oxidation state of the metal atoms were analysed as above, with the composition [Ru$(bzimpy_{-H})$(bpy)(pyz)(bpy)$(bzimpy_{-H})$Ru][$(PF_6)_3$] and [Ru$(bzimpy_{-H})$(phen)(pyz)(phen)$(bzimpy_{-H})$Ru][$(PF_6)_3$] (pyz = pyrazine) [100]. However, the formulae of the complexes could equally well be rewritten as [{Ru$(bzimpy_{-H})$(bpy)}$_2$(μ-pyz)][$(PF_6)_3$] and [Ru$(bzimpy_{-H})$(phen)}$_2$(μ-pyz)Ru][$(PF_6)_3$], respectively. Bioactive behaviour of these complexes was investigated by luminescence activity. Luminescence was quenched by addition of calf-thymus DNA to the complexes.

Two mixed ligand complexes [Ru$(bzimpy_{-H})L^{a1}$DMSO]$(PF_6)_2$ and [$Ru_2(bzimpy_{-H})_2L^{a2}Cl_2$]$(PF_6)_2$ (L^{a1}, L^{a2} = aryl-azo pentane-2,4-dione ligands) [101] were characterized by IR, ^{1}H NMR UV/vis and EPR spectroscopy. Antibacterial, antitumor and anti-HIV properties were also determined.

A complex [Ru(bzimpy)Cl_3] was synthesized [102] as a precursor for some Ru(II) complexes.

3.1.5. *d^6 systems – Fe(II), Ru(II), Co(III), Rh(III), Ir(III), Re(I) (d^5s^1)*

Based on magnetic data for the complex [Fe(bzimpy)Cl_2] its real structure was suggested to be [Fe$(bzimpy)_2$][$FeCl_4$] [29] in which the cation and anion are purely low and high spin, respectively.

The magnetic moment of the complex (Fe$(bzimpy)_2$(Cl_2·MeOH lies in the range of 0.8 μ_B at 10 K to 2.2 μ_B at 300 K. The authors explained this fact in terms of the temperature-independent paramagnetism (or it could be due to impurities of Fe(III)) [29].

Complexes with different water content were prepared [Fe$(bzimpy)_2$]$(ClO_4)_2$·nH_2O (n = 0–1). Some of them seem to be in LS state some of them in HS state and some of them exhibit spin crossover phenomenon. For that reason all of them are discussed in Section 3.1.5.1.

The complex [Fe$(bzimpy)_2$]$(CF_3SO_3)_2$·H_2O is LS at 295 K [80]. However, the spin transition cannot be excluded over room temperature (see Section 3.1.5.1). The crystal structure of the complex [Fe$(bzimpy)_2$]$(CF_3SO_3)_2$·2EtOH confirmed the expected structure with two meridionally coordinated ligands to the central atom. The chromophore {FeN_6} forms a pseudo-octahedron. The bond

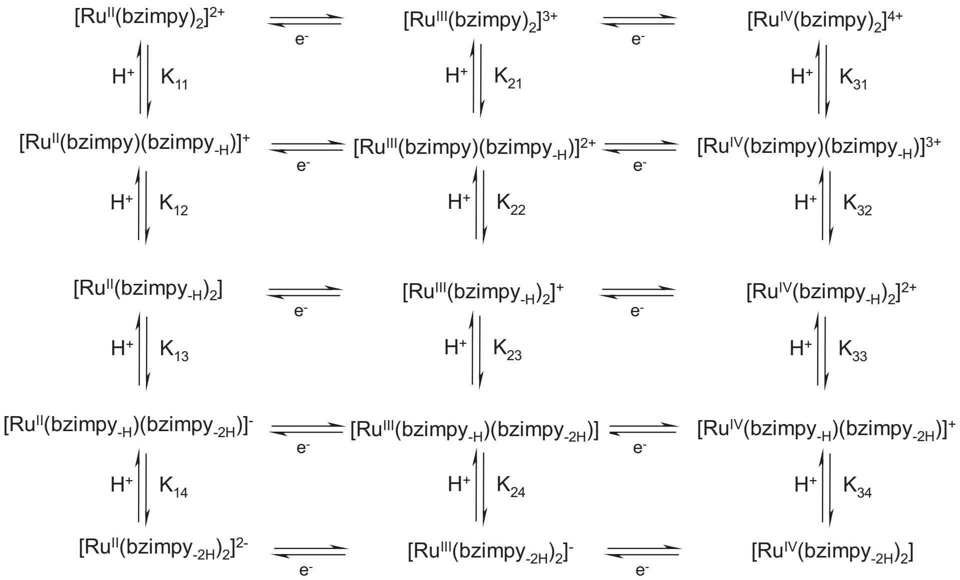


Fig. 12. Possible NH dissociation reactions at different oxidation states of Ru-bzimpy complexes.

lengths of Fe–N_{py} are shorter than that of Fe–N_{bzim}. Moreover, an extensive hydrogen bond network was identified. Unfortunately, no magnetic data are known for the last complex and so a comparison with its hydrate analogue in terms of magnetic properties is not possible.

The complex $[Ru(bzimpy)_2]Cl_2$ was synthesized as a model compound for a Ru(II) polymer complex. This polymer consists of ligands *bzimpy* connected through the position 5- on the benzene ring. After complexation of the polymeric ligand the photosensitivity was enhanced while no electroluminescence was observed in the polymeric complex [102].

Moreover, the ruthenium(II) chloride complex also shows no deprotonation of the ligand as is the case of the chromium(III) [85] and cobalt(II) [103] complexes but provides a bis-complex $[Ru(bzimpy)_2]Cl_2$ [104]. Binding to DNA is of surface mode.

In *trans*-$[Ru(PPh_3)_2(bzimpy)Cl]Cl{\cdot}CHCl_3{\cdot}H_2O$ the molecular components (X-ray) [105] are connected by strong intermolecular hydrogen bonding to form an infinite double column. Each uncoordinated chloride ion forms four acceptor hydrogen bonds, two with adjacent water molecules and one each with the N–H group of an imidazole ligand and a chloroform molecule. A summary of Ru(III)/Ru(II) potentials of the related complexes is given.

Compounds of formula $[RuL(bzimpy)](PF_6)_2$ where the L are different ligands based on *bzimpy* on which proton-coupled electron-transfer reactions were investigated [106]. The self-assembled Ru complex monolayers are polycrystalline on a gold surface where they exhibit a quasi-reversible Ru(III/II) oxidation-proton-coupled electron-transfer reaction. This work was further extended by using an indium thin oxide electrode to study an extended system of the complexes [107]: $[Ru(bizmpy\text{-}X)(bizmpy)](PF_6)_2$ and binuclear complexes $[Os(bzimpy\text{-}X)(btpb)M(bzimpy)](PF_6)_4$ (M = Ru or Os; btpb = 1,4-bis(terpyridyl)benzene, with disulfide (X = S) or with a phosphonic acid ($X = PO_3H_2$) anchoring group).

Proton-linked redox processes of the complex were studied on the complex cation $(Ru(bzimpy)_2(^{2+}$ (from $[Ru(bzimpy)_2](PF_6)_2$) by NMR, UV/vis and electrochemical techniques [58]. The $(Ru(bzimpy)_2(^{2+}$ acts as a tetrabasic acid with pK_a in the range of 2.5–10.7 depending on the ruthenium oxidation state (II–IV). Fig. 12 summarizes the possible NH dissociation reactions at different oxidation states and corresponding pK_a values are summarized in Table 2. (The pK_a value for the free ligand *bzimpy* for the dissociation of the first proton is 11.5 ± 0.1.)

Mixed ligand complexes of Ru(II) were prepared with the following compositions: $[Ru(trpy)(bzimpy)](ClO_4)_2{\cdot}2H_2O$ and $[Ru(trpy)(bzimpy_{-2H})]{\cdot}2H_2O$ (trpy = 2,2′:6′2″-terpyridine) [108]. The first compound replaced two water molecules with one methanol molecule upon recrystallization. The conversion between both complexes was studied by ^1H NMR spectroscopy and electrochemical measurements. The complex with the neutral ligand *bzimpy* converts to the complex with fully deprotonated ligand and *vice versa*. pK_a values of the complexes were determined by a UV/vis method and compared with similar complexes.

Two mixed ligand complexes of ruthenium(II), $[Ru(bzimpy)(bpy)(OH_2)](ClO_4)_2$ and $[Ru(bzimpy)(phen)(OH_2)](ClO_4)_2$ were synthesized and characterized by mass and ^1H NMR spectroscopy, cyclic voltammetry and spectroelectrochemical measurements [109]. For the synthesis a precursor [Ru(bzimpy)(bpy)Cl]Cl or [Ru(bzimpy)(phen)Cl]Cl was used. The proton dissociation constants (pK_a) of both complexes $[Ru(bzimpy)(bpy)(OH_2)](ClO_4)_2$ and $[Ru(bzimpy)(phen)(OH_2)](ClO_4)_2$ were 8.2 and 8.4, respectively. Controlled potential electrolysis of these complexes results in the conversion of ruthenium(II) to ruthenium(III) at 0.6 V and ruthenium(III) to ruthenium(IV) at 0.8 V *vs.* SCE. The binding constant of these complexes with DNA has been determined electrochemically. Viscosity measurements suggest that these complexes bind with DNA through intercalation. Such intercalative binding to DNA induces chirality in the two complexes.

The coordinated molecules of acetonitrile in mixed ligand complex of the composition $[Ru(bzimpy_{-2H})L(CH_3CN)]$ (L = o-phenylenediamine) [110] undergo reduction to ethylamine in the presence of p-phenylenediamine or hydroquinone forming the complex $[Ru(bzimpy_{-2H})L(CH_3CH_2NH_2)]$. This was also supported

Table 2
pK_a values of coordinated ligands in ruthenium complexes based on electrochemical measurements.

n	1	2	3	4	pH range
pK_{1n}	6.1	7.8	9.1	10.7	2.5–10.7
	6.42[a]	7.20[a]	8.7[a]	11.0[a]	4.0–10.7
pK_{2n}	2.5	3.2	5.1	6.2	0–12
pK_{3n}	<0	<0	<2	3.1	0–12

[a] The values obtained spectrophotometrically.

by ^1H NMR studies. The ligand *bzimpy* is present in the dianionic form and thus the proper notation of the ligand in the complexes should be *bzimpy*$_{-2H}$ instead of *bzimpy* (used in the original work). The ligand o-phenylenediamine is present in neutral iminoquinone form. Other complexes with deprotonated ligand *bzimpy* were isolated as $[\mathrm{Ru(bzimpy_{-H})_2}]$ and $[\mathrm{Ru(bzimpy_{-H})(bpy)Cl}]$ [100].

The possibility of tuning the redox potentials and visible absorption band was demonstrated by the series of mixed ligand ruthenium(II) complexes with *bzimpy* *trans*-$[\mathrm{Ru(PPh_3)_2(bzimpy)Cl]Cl}$, *trans*-$[\mathrm{Ru(PPh_3)_2(bzimpy)(CH_3CN)](ClO_4)_2{\cdot}2H_2O}$, $[\mathrm{Ru(bpy)(bzimpy)Cl](ClO_4)}$, $[\mathrm{Ru(terpy)(bzimpy)](ClO_4)_2}$, respectively [111]. In the complex *trans*-$[\mathrm{Ru(PPh_3)_2(bzimpy)(CH_3CN)](ClO_4)_2{\cdot}2H_2O}$ the position of $\mathrm{PPh_3}$ groups is *trans* to each other. The equatorial plane is occupied by coordinated nitrogen atoms of the ligand *bzimpy* and a nitrogen atom from acetonitrile. The identified hydrogen bond network connects the ruthenium complexes into an infinite double chain similarly to that observed in the complex trans-$[\mathrm{Ru(PPh_3)_2(bzimpy)Cl]Cl{\cdot}CHCl_3{\cdot}H_2O}$ [105]. Single crystals of the complex $[\mathrm{Ru(bpy)(bzimpy)Cl](ClO_4)}$ were obtained containing half a molecule of diethylether. Intermolecular H-bonds lead to the formation of H-bonded dimers in the solid state. In $[\mathrm{Ru(terpy)(bzimpy)](ClO_4)_2}$ the ruthenium centre is surrounded by six N donor atoms from the two tridentate ligands with a distorted octahedral geometry. The complexes show absorption at 402–517 nm. This indicates the possibility to tune the visible region absorption by varying the ancillary ligand. Luminescence of the complexes has been observed (LNT). Luminescence behaviour, studied both at room temperature and at liquid nitrogen temperature, of the complexes is insensitive to the presence of dioxygen. Two of the complexes $[\mathrm{Ru(bpy)(bzimpy)Cl](ClO_4)}$ and $[\mathrm{Ru(terpy)(bzimpy)](ClO_4)_2}$ seem to be suitable for application as NIR emitters in solid state devices [111].

In the complex $[\mathrm{Ru(NO_2)(bzimpy)(PPh_3)_2](ClO_4){\cdot}EtOH}$ [112] the *bzimpy*, nitro group and two triphenylphosphine coordinate to the central atom in a pseudo-octahedral manner. Both triphenylphosphine groups are in *trans* position to each other. Analogously to other structures, the bond length of $\mathrm{Fe{-}N_{py}}$ is shorter than the bond lengths of $\mathrm{Fe{-}N_{bzim}}$. The $\mathrm{NO_2}$ plane is rotated by 40.5° from the plane defined by the three nitrogen atoms of the *bzimpy* and Ru. Hydrogen bond interactions were also observed.

For NMR investigation the complex $[\mathrm{Co(bzimpy_{-H})_2]OH}$ was prepared [34]. Two acid hydrogen atoms are in equilibrium between all four uncoordinated imidazole nitrogen atoms from two strongly coordinated ligands.

An extended series of ruthenium and iridium complexes with *bzimpy* were prepared [23]: $\mathrm{RhX_3(bzimpy)}$ (X = Cl, Br, I); $[\mathrm{Rh(bzimpy)_2(OClO_3)](ClO_4)_2}$; $\mathrm{RhX(CO)_2(bzimpy){\cdot}1.5H_2O}$ (X = Cl, Br); $\mathrm{Rh(bzimpy)(CO)_2(OClO_3)}$; $[\mathrm{RhX_2(CO)(bzimpy)]X}$ (X = Cl, Br); $\mathrm{IrX_3(bzimpy)}$ (X = Cl, Br); $\mathrm{IrX(CO)_2(bzimpy){\cdot}}n\mathrm{H_2O}$ (X = Cl, n = 1; X = Br, n = 1.5). An interesting observation was that two different oxidation states (I and III) were found in the complexes. Chloro- and bromo- complexes of rhodium are diamagnetic and undergo decarbonylation in alcohol, 2-methoxyethanol and DMF forming $\mathrm{RhX(L){\cdot}2H_2O}$ complexes. Carbonylation of these complexes resulted in the formation of the parent carbonyls. It is interesting that reversible decarbonylation/carbonylation was observed according to the following scheme:

$$[\mathrm{Rh}(\mathit{bzimpy})(\mathrm{CO})_2\mathrm{X}]\underset{+\mathrm{CO}}{\overset{-\mathrm{CO}}{\rightleftharpoons}}[\mathrm{Rh}(\mathit{bzimpy})\mathrm{X}]$$

Here the question can arise as to whether a protonation/deprotonation reaction can occur instead of a redox process. The above authors do not provide any information about N–H vibrations in IR spectra and moreover it is not clear whether absence of NMR measurements of Rh(I) and Ir(I) complexes arise from the authors preposition of oxidation state I or from really no relevant signal being obtained as can be expected for Rh(I) and Ir(I) complexes due to unpaired electrons. Bidentate behaviour of the ligands in some complexes was also discussed. See also [113].

3.1.5.1. Spin crossover phenomenon. It was mentioned in the previous section that the transition metal complexes with a specific electronic configuration enabling the LS to HS spin transition belong to materials with high potential of industrial application. This was one of the reasons why we focused our attention on the materials where spin crossover was expected, in a separate section.

Recent research indicates that spin crossover can be affected by various factors responsible for mutual interactions of the complex units in the solid state. Hydrogen-bonding networks or van der Waals interactions belong to these and thus the ligands, counterions or uncoordinated solvent molecules can be involved in such interaction.

On the basis of our experience and literature data the following effects should be taken into consideration when studying the hydrogen bonds and their consequences to magnetic properties of the complexes:

- the method used for the preparation of the complex – a different stoichiometry of the complexes with variable content of solvates could be obtained;
- variation of the counter ions can lead to different hydrogen bonding networks;
- substitution of the ligand with various functional groups may manifest itself in different solid-state interactions.

On the other hand, the study of the complexes with different central atoms can provide important information about the effect of the ligands itself on the properties of the complexes.

In the spin crossover systems containing Fe(II) the transition from LS to HS is accompanied with an increase of the Fe–N bond length of about 0.14–0.23 Å. Moreover, if the spin transition is kinetically slow (k = 4.10^5–$3.10^8\ \mathrm{s^{-1}}$), and comparable with exciting of a vibrational mode, the LS and HS states can be easily detected by infrared spectroscopy [114,115]. There is a variety of publications describing this phenomenon from different points of view [116–128].

In the following section a review of literature data on $[\mathrm{Fe(bzimpy)_2](ClO_4)_2{\cdot}}n\mathrm{H_2O}$ (n = 0–1) is presented. As can be seen different techniques can be useful for spin crossover monitoring and the content of solvent molecules seems to be crucial in determining magnetic properties.

Values of the magnetic moment of the $[\mathrm{Fe(bzimpy)_2](ClO_4)_2}$ complex measured on SQUID are in the range of 0.6 μ_B at 6 K and 2.8 μ_B at 300 K [29] (the amount of crystal solvent molecules and amount of Fe(III) impurities are not reported, if present at all). It was observed that the LS state of the complex can be excited by irradiation with visible light and decay of the resulting HS form can be observed under cryogenic conditions. It seems to be the first example of the phenomena called LIESST (Light Induced Excited Spin State Trapping [129]) for complexes with the ligand *bzimpy*. The spin crossover of this complex was monitored by far-IR spectra in the temperature range of 93–343 K [35,36] and by UV/vis in the range of 276–331 K [33]. The ν_LS(Fe–N) vibrations, around 436 $\mathrm{cm^{-1}}$, were shifted to higher frequencies on cooling whilst the ν_HS(Fe–N) vibrations, around 281 $\mathrm{cm^{-1}}$, were shifted to lower frequencies on heating as the Fe–N bond was weakened. The equilibrium constant K_SCO was determined as a ratio of intensities $I_\mathrm{HS}/I_\mathrm{LS}$ [35], but a correct determination of K_SCO requires integral areas instead of intensities to be applied. Upon applying higher temperature range, 100 K and 520 K, hysteresis loops in both CsI

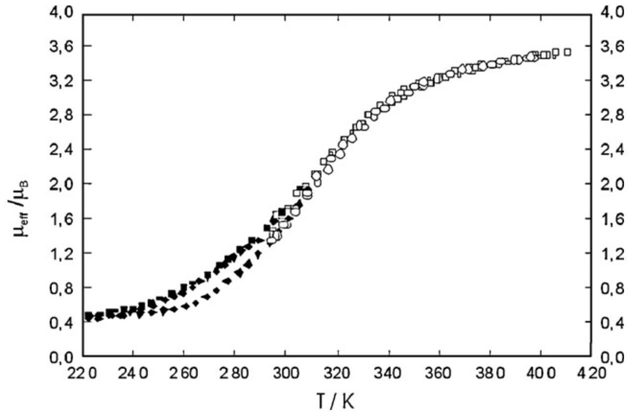


Fig. 13. The effective magnetic moment μ_{eff}/μ_B of (Fe(bzimpy)$_2$((ClO$_4$)$_2$·0.25H$_2$O on heating/cooling (Faraday balance data). According to [133] with kind permission from the publisher.

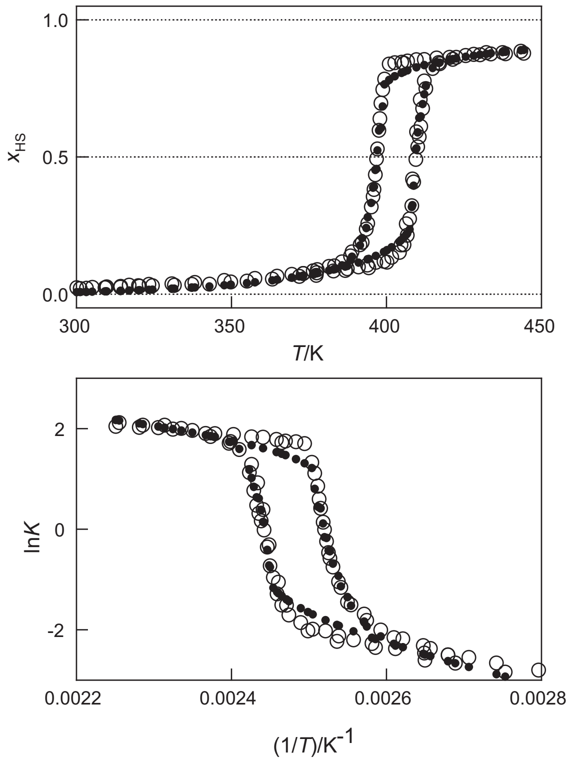


Fig. 14. High-spin mole fraction (top) and van't Hoff plot (bottom) for (Fe(bzimpy)$_2$((ClO$_4$)$_2$·0.25H$_2$O: experimental (open circles) and theoretical (full points). According to [31] with kind permission from the publisher.

and polyethylene matrices appeared. The hysteresis broadening is dependent on the matrix and is bigger in CsI [130].

The temperature dependence of the effective magnetic moment of the complex [Fe(bzimpy)$_2$](ClO$_4$)$_2$ in different solvents, determined by ^{1}H NMR, was monitored [131]. The values are higher than in the solid state, and this was explained as being due to antiferromagnetic or similar coupling effect. DSC data [132] provided the values of thermodynamic quantities as high as ΔH = 15.4 kJ mol^{-1} and ΔS = 40.0 J K^{-1} mol^{-1} for the low-spin to high-spin transition.

[Fe(bzimpy)$_2$](ClO$_4$)$_2$ diffused into a poly(vinyl)alcohol polymer matrix exhibits a thermally induced spin crossover with anisotropic effect after stretching. After stretching the matrix, the compound orients itself in the matrix. Polarised UV/vis spectra measured parallel and perpendicular to the stretching direction allowed one to calculate the distortion of the molecule in the matrix by means of semi-empirical PPP SCF-CI calculations [50]. When the complex was added to PVA, the bordeaux-red colour almost instantly disappeared.

An anhydrous complex was also reported by [59] but was not characterized. The monohydrate complex [Fe(bzimpy)$_2$](ClO$_4$)$_2$·H$_2$O [80] is LS at room temperature based on Mössbauer spectra.

Probably the most frequently investigated spin crossover system is [Fe(bzimpy)$_2$](ClO$_4$)$_2$·0.25H$_2$O. Different values of the magnetic moment for the complex (Fe(bzimpy)$_2$((ClO$_4$)$_2$·0.25H$_2$O were recorded using different techniques [133]. On an AC susceptometer (B = 0.001 T) magnetic moments ranged between 1.37 μ_B at 83 K to 3.01 μ_B at 310 K on Faraday balance (B = 1.3–1.5 T) between 0.21 μ_B at 7.5 K and 3.53 μ_B at 410 K. On heating/cooling regime visible hysteresis appeared (Fig. 13) which, moreover, is field and time dependent (the system needs some time to reach equilibrium). On sample ageing, part of Fe(II) is oxidized to Fe(III) as was monitored by magnetic measurements, UV and EPR [133,134]. The effective magnetic moment (belonging to LS state) at 80 K increases from 0.3 μ_B for a freshly prepared sample to 1.2 μ_B for one-year old sample [133].

The value of J/k = −232 K indicates the existence of strong cooperativity and it can be visualized as a substantial non-linearity in the vant' Hoff plot of ln K_{SCO} *vs.* 1/T [135]. From the temperature-dependent IR spectra a complete LS to HS transition can be estimated at 520 K [133]. The X-ray structural analysis reveals that the central atom is coordinated by six nitrogen atoms; the ligands are perpendicular to each other. The equatorial plane is formed by four imidazole nitrogen atoms and shows a slight tetrahedral distortion. Pyridine nitrogen atoms occupy axial positions so that a bipyramidal structure is formed [133]. Bond distances Fe–N$_{py}$ are shorter than Fe–N$_{bzim}$ ones, however both are shorter than those in the complex [Fe(bzimpy)$_2$](CF$_3$SO$_3$)$_2$·2EtOH. A weak hydrogen-bond interaction between the imidazole hydrogen atom and an oxygen atom of the perchlorate group exists; moreover HOH...OClO$_3$ interaction exists in the solid state as well.

Detailed procedure of fitting the magnetic data to the two-level Ising-like model with and without molecular vibrations for the complex (Fe(bzimpy)$_2$((ClO$_4$)$_2$·0.25H$_2$O is given in [136]. The idea of two-step spin crossover was introduced for this complex. The first step is rather continuous: it starts at 200 K and culminates at 330 K. The second step is very sharp and accompanied by a hysteresis: $T_c^{\uparrow} = 405$ K, $T_c^{\downarrow} = 397$ K. The existence of the hysteresis is conditioned by a considerable ferromagnetic coupling for one of the sublattices ($J_A/k \approx 900$ K).

Careful reinvestigation of this system [31] revealed that the system exhibits an abrupt low-spin to high-spin transition at T_c = 403 K. Liberation of a fractional amount of water does not affect the spin crossover: the system is perfectly reversible with a hysteresis width of ΔT = 12 K (Fig. 14).

The existence of the hysteresis at such high temperature strongly suggests that the lowest limit of the solid-state cooperativity parameter is J/k > 403 K despite long iron(II) separations (~10 Å). High cooperativity has been ascribed to a perfect π-stacking of the benzimidazole rings in the crystal lattice at a distance as short as 3.6 Å. Variable-temperature IR data (Fig. 15) and the heat capacity measurements match well the magnetic data. The thermodynamic properties are ΔH = 17 kJ mol^{-1}, ΔS = 43 J K^{-1} mol^{-1}, so that the entropy of the spin transition shows a considerable contribution from molecular vibrations. A theoretical model has been applied in fitting the magnetic data along the whole hysteresis path. A statistical distribution of the cooperativity parameter led to the feature that angled walls of the hysteresis loop are well reproduced [31].

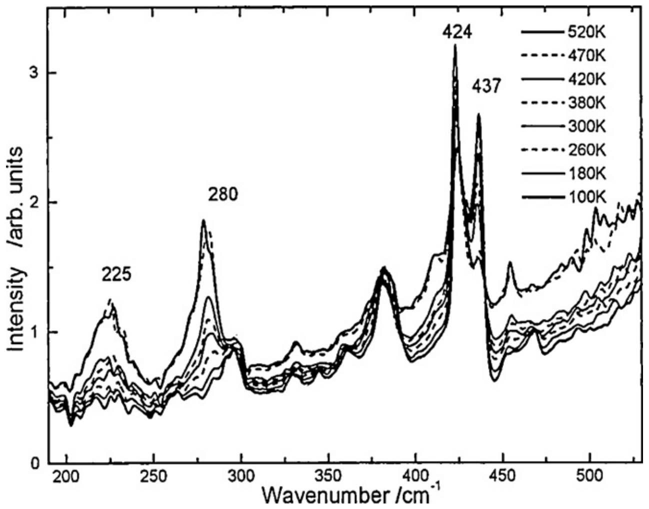


Fig. 15. FT-IR spectra of $(Fe(bzimpy)_2((ClO_4)_2\cdot 0.25H_2O$ on heating. According to [31] with kind permission from the publisher.

With the complex above, the need for some new theoretical models was demonstrated [137] together with the review of other models.

The complex $[Fe(bzimpy_{-H})_2]\cdot H_2O$ was characterized by only UV/vis spectra in $CH_3OCH_2CH_2OH$ [29]. Another hydrate as $[Fe(bzimpy_{-H})_2]\cdot 0.5H_2O$ is in LS state at room temperature in the solid state based on UV/vis [80].

The complex $[Fe(bzimpy_{-H})_2]\cdot 2H_2O$ showed a spin transition from LS to HS above room temperature. The transition temperature is higher than that for the corresponding non-deprotonated complex. A very broad hysteresis loop was observed [138]. Later, the same complex was referred to as monohydrate $[Fe(bzimpy_{-H})_2]\cdot H_2O$ [139] and this was confirmed by structural analysis. The two benzene rings, R1 and R2, belonging to the neighbouring molecular units show perfect π-stacking with the detail that each carbon atom of R1 lies just above the centre of the C–C linkage of R2; the ring separation is only 3.59 Å (Fig. 16).

The magnetic properties of $[Fe(bzimpy_{-H})_2]\cdot H_2O$ exhibit a more complex temperature variation. The effective magnetic moment rises from its room-temperature value $\mu_{eff} = 1.8\,\mu_B$ to $\mu_{eff} = 4.2\,\mu_B$ at the limit of the heating (500 K) [139] (Fig. 17). The liberation of the crystal water was observed at higher temperatures.

The high value of $\Delta H = 18\,\text{kJ mol}^{-1}$ and moderate $\Delta S = 43\,\text{J K}^{-1}\,\text{mol}^{-1}$ explain a high value of $T_c = \Delta H/\Delta S = 424\,\text{K}$ shifted far above room temperature. This value matches the calorimetric readings $T_{p1}^{\uparrow} = 424\,\text{K}$ [140]. A "broad hysteresis" is visible between 300 K and 500 K for $[Fe(bzimpy_{-H})_2]\cdot H_2O$. However, the hysteresis width is only a few K when measured at its centre. This behaviour is similar to that of $(Fe(bzimpy)_2((ClO_4)_2\cdot 0.25H_2O$ where a "broad hysteresis" was observed [133]. Such an effect originates either in the distribution of the domain sizes, or in a statistical degradation of the cooperativity due to a partial oxidation during its aging, or an appearance of defects owing to crystal water liberation [31].

Spin crossover phenomenon on $[Fe(bzimpy)_2](ClO_4)_2\cdot 0.25H_2O$ and $[Fe(bzimpy_{-H})_2]\cdot H_2O$ was investigated by a DSC method [140]. The DSC data correspond to a first-order phase transition. The transition temperatures obtained correspond to those derived from temperature dependent magnetic susceptibility measurements. For the first complex obtained values are in the range of $\Delta H = 14\text{–}17\,\text{kJ mol}^{-1}$ and of $\Delta S = 35\text{–}43\,\text{J mol}^{-1}\,\text{K}^{-1}$ for two different cooling cycles. In addition, some hysteresis was observed corresponding to magnetic measurements. For both complexes the liberation of crystal water was observed at higher a temperature which was also confirmed by temperature dependent X-ray powder patterns and temperature dependent IR spectroscopy measurements.

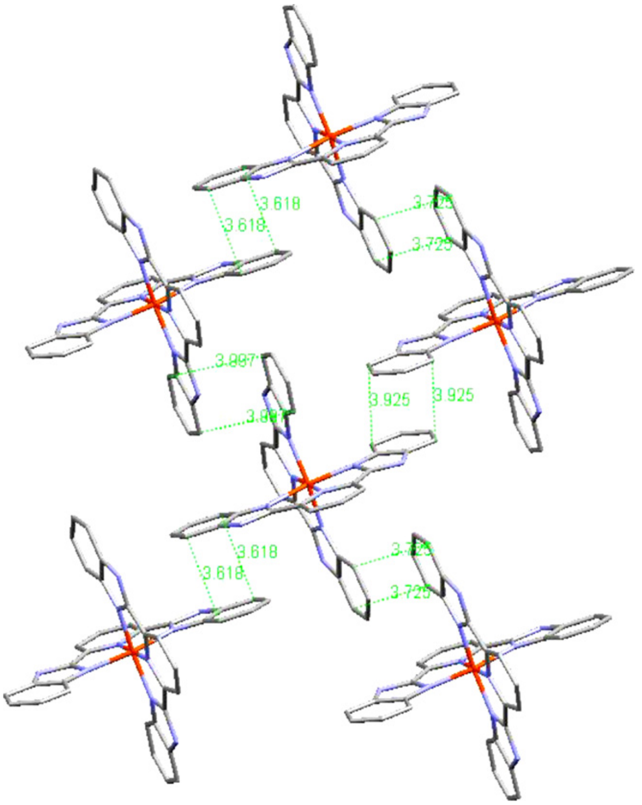


Fig. 16. Crystal structure of $[Fe(bzimpy_{-H})_2]\cdot H_2O$ showing π-stacking of the benzene rings.

Spin crossover behaviour of the deprotonated complex $[Fe(bzimpy_{-H})_2]\cdot H_2O$ was monitored also by complementary techniques UV/vis and IR spectroscopy over the temperature range 180–520 K [141] providing $\Delta H = 13.3\,\text{kJ mol}^{-1}$ and $\Delta S = 42.5\,\text{J mol}^{-1}\,\text{K}^{-1}$. The transition temperature was estimated at

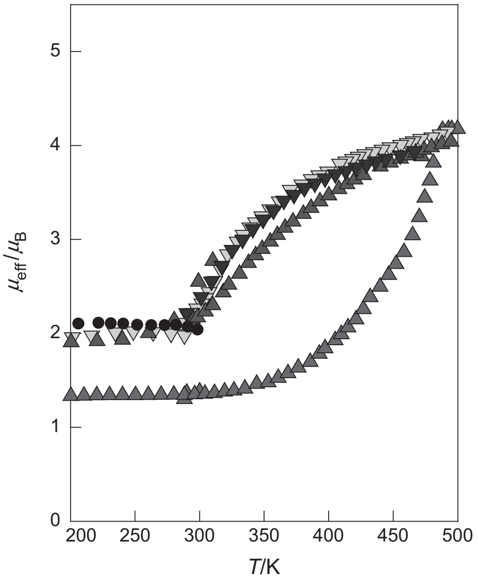


Fig. 17. Temperature dependence of the effective magnetic moment for $[Fe(bzimpy_{-H})_2]\cdot H_2O$ over different temperature regimes. According to [139] with kind permission from the publisher.

380 ± 40 K. However, Mössbauer spectra recorded up to 300 K did not show any spin transition.

Fluorescence properties of the complexes $[Fe(bzimpy)_2](ClO_4)_2$ and $[Fe(bzimpy_{-H})_2]$ were investigated [61]. The deprotonated complex $[Fe(bzimpy_{-H})_2]$ in methanol fluoresces from both spin states and their ratio is temperature dependent (amount of HS increases with increasing temperature). For the complex $[Fe(bzimpy)_2](ClO_4)_2$ in methanol similar results were obtained. Using the Boltzmann equation the calculated ratio of both spin states was in excellent agreement with the data obtained by other techniques.

Analogous complexes to the perchlorate ones were prepared using the tetraphenylborate anion $(Fe(bzimpy)_2((BPh_4)_2{\cdot}nH_2O$ ($n = 4, 2, 0$). The presence and amount of crystal water was detected by temperature-dependent IR spectra and thermogravimetric measurements. The complex with $n = 4$ alters to the anhydrous complex at $T = 313–323$ K [30]. The tetrahydrate is a spin crossover system with the complete transition centred at room temperature. The dihydrate, prepared from a solution with reduced water content, is a high-spin complex over the entire temperature region. The anhydrous complex, prepared by overheating the tetrahydrate, remains high-spin. The magnetic data fitting procedure for the tetrahydrate complex yields a set of magnetic parameters describing the spin crossover quantitatively: $g = 2.54$, $J/k = -226$ K, $\Delta H = 14.9\ \mathrm{kJ\ mol^{-1}}$ and $\Delta S = 45\ \mathrm{J\ K^{-1}\ mol^{-1}}$. Investigation of the system by temperature dependent IR spectra correlates with the data from magnetic measurements, where the molar ratio of HS state was compared. The molar ratio of HS from Ir spectra was calculated according to the equation:

$$c_{HS}^{T} = 1 - c_{LS}^{T} = 1 - \frac{A - A_0}{A_{LS} - A_0}$$

where A_{LS} is the area fraction associated with the low-spin state vibration ($\tilde{\nu}(\mathrm{Fe–N}) = 440\ \mathrm{cm^{-1}}$) of the complex and A_0 is the residual area fraction as an effect of the presence of other overlapping vibrations and eventually the high-spin portion [30]. Detailed procedure of fitting the magnetic data to the two-level Ising-like model with and without molecular vibrations for the complex $(Fe(bzimpy)_2((BPh_4)_2{\cdot}4H_2O$ is given in [136]. The complex $(Fe(bzimpy)_2((SO_4)_2{\cdot}2H_2O$ shows features of spin crossover, but the conversion is far from being complete at 550 K [30].

In Table 3 important thermodynamic data are summarized for different spin crossover systems of the ligand *bzimpy* obtained by different techniques. The enthalpy and the entropy change associated with the spin transition can be obtained by processing the calorimetric data (by integrating heat capacity). However, the theoretical models of the spin crossover allow calculation of ΔH and ΔS on the basis of the conversion curve $x_{HS} = f(T)$ (x_{HS} is molar fraction of the high spin state). A regular solution model, or eventually other models of the spin crossover, can be applied to the data produced by magnetic susceptibility measurements, Far-IR data and Mössbauer spectral data; in addition, the EXAFS and powder X-ray data have also been utilized for this purpose.

Different kinds of substitution, such as replacement of the hydrogen atom on the imine nitrogen atom by the methyl group, can enrich our knowledge about factors influencing spin crossover. An alternative way of studying the Fe(II) complexes with the ligand *bzimpy* would be substitutions in position 4- of the pyridine ring. However, this is beyond the scope of this Paper.

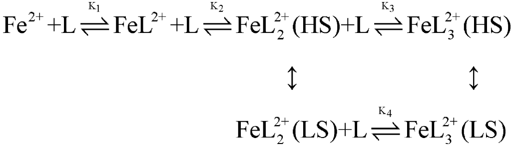
3.1.5.2. Solution investigation. An extended study of the spin-state equilibrium of the $[Fe(bzimpy)_2]^{2+}$ in solution was made [29,32,33,141–147].

In solution the complex cation $[Fe(bzimpy)_2]^{2+}$ acts as a weak diprotic acid and the spin transition can be observed (in CH_3CN the following data were obtained: $\Delta H^{\theta} = -42.7\ \mathrm{kJ\ mol^{-1}}$, $\Delta S^{\theta} = -140.9\ \mathrm{J\ K^{-1}\ mol^{-1}}$ [29]).

The spin crossover phenomenon of iron(II) and *bzimpy* in non-aqueous solution was investigated in terms of complex formation constants [142]. The ligand *bzimpy* can act as a tridentate ligand towards Fe(II) in methanol at 20 °C forming $[Fe(bzimpy)]^{2+}$ ($\log K_1 = 5.54$), $[Fe(bzimpy)_2]^{2+}$ ($\log K_2 = 4.12$). The ligand can also act as a bidentate one forming $[Fe(bzimpy)_3]^{2+}$ ($\log K_3 = 3.85$). The thermodynamic parameters for spin equilibrium in solution for the reaction:

$$FeL_3^{2+}(LS) \rightleftharpoons FeL_3^{2+}(HS)$$

are $\Delta H = 17.7\ \mathrm{kJ\ mol^{-1}}$, $\Delta S = 59.0\ \mathrm{J\ mol^{-1}\ K^{-1}}$ (see Table 4). The following general equilibrium scheme was suggested



$$\begin{tikzcd} Fe^{2+} + L \arrow[r, "K_1", shift left=0] & FeL^{2+} + L \arrow[r, "K_2"] & FeL_2^{2+}(HS) + L \arrow[r, "K_3"] \arrow[d, leftrightarrow] & FeL_3^{2+}(HS) \arrow[d, leftrightarrow] \\ & & FeL_2^{2+}(LS) + L \arrow[r, "K_4"] & FeL_3^{2+}(LS) \end{tikzcd}$$

in which both HS species can undergo a spin transition to LS upon cooling. Moreover, a pronounced thermochromism was observed as a result of the spin crossover phenomenon and dissociation equilibrium. Addition of triethylamine causes removal of acidic hydrogen.

However, two critical assumptions were made in the above work: the authors simply expected the formation of the complex M:L 1:3 based on a comparison with the ligands 1,10-phenantroline, 2,2′-bipyridyl and 2,2′-pyridylimidazole that are two-functional ligands. Consequently, complexes of the metal to ligand ratio 1:3 can easily be formed, in contrast to *bzimpy* which is three-functional. They presume that in the case of the complex $[Fe(bzimpy)_3]^{2+}$ the ligands behave as two-functional ones. Moreover, they stated that the electronic environment around the Fe^{2+} core was similar to that found in $[Fe(bzimpy)_2]^{2+}$ and $[Fe(bzimpy)_3]^{2+}$. This has, however, no physical support. In the case of $[Fe(bzimpy)_3]^{2+}$ the environment around the iron(II) could be similar to that depicted in Fig. 18.

A theoretical calculation supporting the existence of the complex with three coordinated ligands *bzimpy* is still missing. It is most likely that steric conditions do not allow the existence of such

Table 3
Thermodynamic parameters of the spin transition obtained by different techniques.

System	Technique	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})	T_c (K)	ΔT (K)	g	J/k (K)	Ref.
$(Fe(bzimpy)_2((ClO_4)_2{\cdot}0.25H_2O$	Magnetic measurements	13.9	34.7	409↑ 397↓				[31,136]
	Theoretical	17.9	44.4	403				[31]
	DSC	17.4	43.1	404	12	2.01	454	[31,139]
	DSC	14–17	35–43	404				[140]
$(Fe(bzimpy)_2((ClO_4)_2$	IR	13.3	42.5					[141]
	DSC	15.4	40.0					[132]
$(Fe(bzimpy)_2((BPh_4)_2{\cdot}4H_2O$	Magnetic measurements	14.9	45.2	330	–	2.54	226	[30,136,139]
$[Fe(bzimpy_{-H})_2]{\cdot}H_2O$	Magnetic measurements	18.1	43	424	–	2.48	519	[139]

Table 4
Thermodynamic parameters of spin crossover for $[Fe(bzimpy)_2]^{2+}$ and $[Fe(bzimpy)_3]^{2+}$.

Solvent	log β_2	ΔH_{SCO} (kJ mol^{-1})	ΔS_{SCO} (J mol^{-1} K^{-1})	$\mu/\mu_{B.M.}$ (temp. range)	Ref.
MeOH[a]	10.7				[145]
MeOH[b]	9.6	17.7[c]	59.0[c]		[142]
MeOH[b,a]		17.0[d]	60.9[d]	3.0 298	[143]
Acetone[b,a]		19.0[d]	71.6[d]	3.9 298	[143]
Acetonitrile[b,a]		21.3[d]	82.9[d]	4.2 298	[143]
Nitromethane[b,a]		18.1[d]	67.3[d]	3.4 298	[143]
PDC[b,a]		19.7[d]	68.3[d]	4.8 298	[143]
MeOH[a]				1.30–2.50–3.40 213–294–328	[32]
Acetonitrile[a]				0.85–4.51 251.7–340.0	[32]
Nitromethane[a]				1.62–4.10 258–343	[32]
MeOH[a]		16.5[c]	54.2[c]		[33]
Dmf[a]		0.9[c]	141.1[c]		[33]
MeOH[a]	10.1	20.5[d]	58.6[d]	1.31–3.34 213.7–328.7	[33]
Acetonitrile[a]		17.4[d]	57.3[d]	1.72–3.88 230.2–328.7	[33]
Acetone[a]		22.5[d]	68.1[d]	0.85–4.51 251.7–340.0	[33]
Nitromethane[a]		20.4[d]	60.8[d]	1.62–4.10 258–343	[33]
PDC[a]		23.9[d]	73.9[d]	0.64–3.46 230.2–306.9	[33]
DMF(20%)/MeOH[a]		29.4[d]	93.1[d]	2.30–3.80 219–317	[33]
PDC(50%)/MeOH[b,a]	10.9–11.5				[147]
PDC(50%)/MeOH[a]	11.5				[145]
PDC(50%)/MeOH[a]		14.7	53.6		[148]
MeOH[a]		22.7[d]	85.1[d]	2.32–5.03 240–320	[141]
MeOH[e]		25.6[d]	92.8[d]	1.65–5.03 240–320	[141]
PDC[a]		18.4[c]	66.9[c]		[146]
PDC[a]		17.6[c]	61.9[c]		[146]
PDC[a]		23.8[d]	75.1[d]	0.69–4.11 232.1–350.5	[146]
PDC		17.4	61.9		[146]
MeOH[a]		16.3[c]	54.0[c]		[146]

PDC—propanediol-1,2-carbonate; DMF—dimethylformamide.

[a] For $FeL_2^{2+}(LS) \rightleftharpoons FeL_2^{2+}(HS)$.

[b] For $FeL_3^{2+}(LS) \rightleftharpoons FeL_3^{2+}(HS)$.

[c] Data from UV/vis.

[d] Data from NMR.

[e] For $[Fe(bzimpy_{-H})_2]$.

a complex. There is no reason why the strongly favoured chelating effect could be reduced from two rings per ligand to only one ring per ligand and, moreover, why introduce strongly disfavoured steric hindrance (e.g. cancellation of conjugation by rotation of one benzimidazol-2-yl group out of the ligand plane because such a state of the *bzimpy* would have a higher energy than the planar molecule [61]). Moreover, it was also claimed that no clear distinction was observed between the UV/vis spectra of $[Fe(bzimpy)_2]^{2+}$ and $[Fe(bzimpy)_3]^{2+}$.

In another study [143], different solvents (methanol, acetonitrile, nitromethane, acetone, propanediol-1,2-carbonate; see Table 4) were used to investigate their influence on the spin equilibrium in $[Fe(bzimpy)_n]^{2+}$ ($n = 1, 2, 3$) by the Evans method using an NMR technique [75]. However, assumption of the existence of $[Fe(bzimpy)_3]^{2+}$ undergoing spin transition remained. Both bis- and tris-ligand complex ions undergo spin crossover simultaneously. It was concluded that increase of solvent donor number (from acetonitrile to methanol) causes a decrease of the HS fraction of complex cation. Further increase of donor number results in deprotonation of the ligand providing a LS species. Similar results were presented elsewhere [32]. It was stressed that the spin crossover behaviour in the above system is strongly sensitive to solvent effects.

The influence of the protonation/deprotonation equilibrium on $[Fe(bzimpy)_2]^{2+}$ was studied by potentiometric titration [144]. A relatively high acidity of the iron complex was revealed. The influence of pH on the spin equilibrium of the $[Fe(bzimpy)_2]^{2+}$ was studied by spectrophotometric titration and by NMR spectroscopic titration. The deprotonation of the ligand in the complex leads to a change of spin state from HS to LS. The potentiometric titration was also examined for Ni(II), Co(II), Mn(II) and Zn(II) complexes.

Dependence of the magnetic moment on the molar ratio L:Fe in different solvents was also investigated by means of NMR [145]. Moreover, spectrophotometric titration of the iron(II) solution with solution of the ligand showed that the complexation was completed after addition of stoichiometric amounts of the ligand for $[Fe(bzimpy)_2]^{2+}$ but only in PDC(50%)/MeOH mixture. In other solvents significant dissociation was observed.

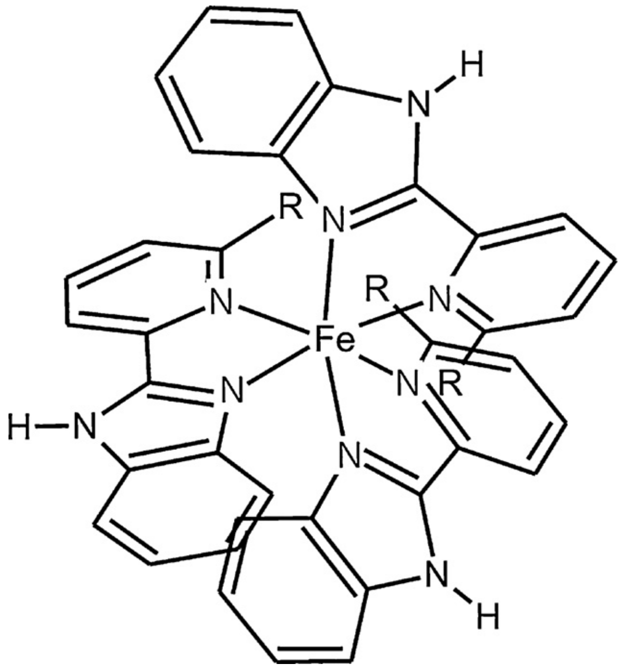


Fig. 18. Sketch of the $[Fe(bzimpy)_3]^{2+}$. Hydrogen atoms on carbon atoms were omitted for clarity, R is the non-coordinated group of benzimidazol-2-yl. Geometry was optimized by MM+ molecular mechanics method using HyperChem 6 [73].

Deprotonation of the ligand was obtained *in situ* by addition of basic solvents. However, the spin transition was also investigated in the solution of the electro neutral $[Fe(bzimpy_{-H})_2]$ complex that was prepared previously as a solid [141]. The obtained thermodynamic parameters (Table 4) are slightly higher than the data for $[Fe(bzimpy)_2]^{2+}$.

The influence of excess ligand on the spin equilibrium of the $[Fe(bzimpy)_2]^{2+}$ in PDC was also investigated. Lower values of thermodynamic parameters were found in the solution with excess of ligand using spectrophotometric measurements. However, the data from NMR measurements are significantly higher [146].

The influence of solvent to spin equilibrium in $[Fe(bzimpy)_2]^{2+}$ was expanded to a study of temperature dependence. Temperature dependence of the formation constants of Fe(II)-bzimpy complex have been investigated in the mixture PDC(50%)/MeOH [147]. The values of formation constant, $\log_{10}\beta_2 = 10.90–11.47$, decrease with increasing temperature over the temperature range 4–32 °C. The thermodynamic parameters for complexation equilibrium are $\Delta H = 50.52\,kJ\,mol^{-1}$, $\Delta S = 43.28\,J\,mol^{-1}\,K^{-1}$. Study at low temperature (4 °C) revealed the formation of the tris-complex $[Fe(bzimpy)_3]^{2+}$. These authors explained the ligand behaviour in the same manner as above [142].

From the above investigation, a general scheme of the different species in solution can be drawn (Fig. 19). It was stated that the species $[Fe(bzimpy)_2]^{2+}$ and $[Fe(bzimpy)_3]^{2+}$ can undergo spin transition on change of temperature. This phenomenon is strongly dependent on the nature of the solvent. The spin state of other species is expected to be LS over the investigated temperature range. For the dependence on molar ratio, counter-anion and other additives only three kind of complex particle were obtained as solids (shown bold in Fig. 19). This scheme is valid for iron(II) but probably a similar scheme could be applicable to iron(III).

The electron availability on the imidazole nitrogen atom is lowered after coordination of the ligand to the central atom because of hyperconjugation. Consequently, the basicity of the benzimidazole hydrogen atom increases. Titration of such a cation by a base results in deprotonation of the imine hydrogen atom and this can have an effect on the spin transition of the complex.

Moreover, in solution the complex $[Fe(bzimpy)_2](ClO_4)_2$ undergoes a considerable dissociation (in DMF, DMSO) – even in the presence of considerable excess of the ligand [80].

According to IR spectra of the complex $[ReBr(CO)_3(bzimpy)]$ [24] in solution (CH_2Cl_2), it was concluded that all three carbonyl groups are coordinated in *fac* fashion. Bidentate behaviour of the ligand (through the pyridine nitrogen and only one benzimidazole nitrogen atom) was also confirmed by NMR investigation. The complex is fluxional with the nitrogen ligand oscillating between equivalent bidentate bonding modes. Activation energy for Re–N fluxions are $\Delta H^{\#} = 72.2(\pm 2.5)\,kJ\,mol^{-1}$, $\Delta S^{\#} = -5.4(\pm 7.1)\,J\,K^{-1}\,mol^{-1}$ (at 298.15 K).

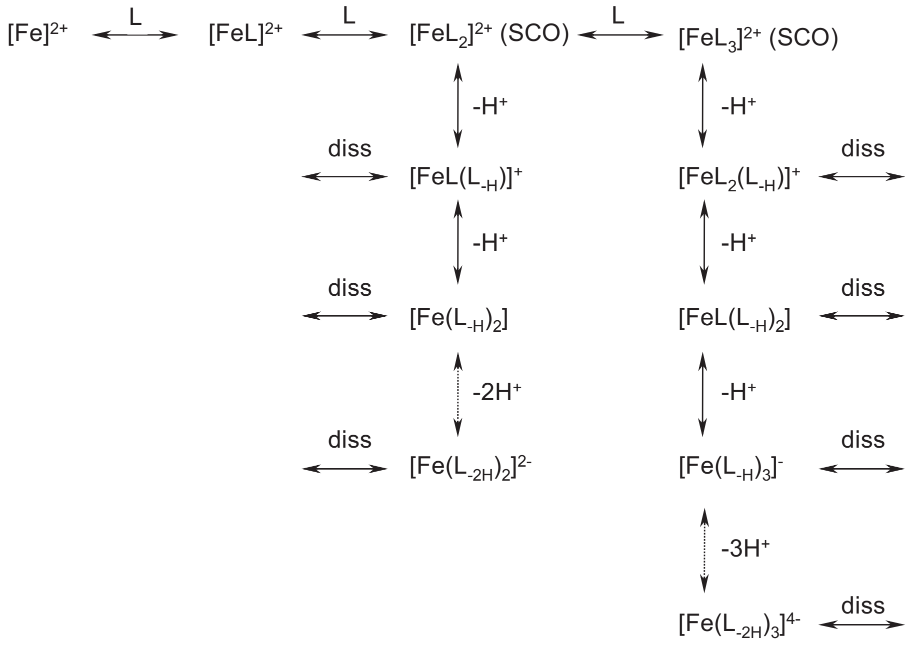


Fig. 19. General scheme of the different species in the solution of the system Fe-bzimpy.

3.1.6. d^7 systems – Co(II)

Temperature variation of the effective magnetic moment for a penta-coordinated [Co(bzimpy)Cl_2] complex shows a pronounced deviation from linearity below 120 K. Quantitative analysis based on the diagonalization of the spin Hamiltonian matrices gave the set of magnetic parameters: $g_x = 2.501$, $g_y = 2.622$, $g_z = 1.476$, $D/hc = 71.7\,\mathrm{cm}^{-1}$, $E/hc = 1.4\,\mathrm{cm}^{-1}$, $\alpha_{\mathrm{TIP}} = 0.98 \times 10^{-9}\,\mathrm{m}^3\,\mathrm{mol}^{-1}$ and $zJ/hc = -0.184\,\mathrm{cm}^{-1}$ SQUID data. The extreme value of the axial zero-field splitting parameter *D* shows that the magnetic anisotropy determined by the non-spherical distribution of the spin density is enhanced by the low symmetry of the penta-coordinate chromophore [92,93].

The complex [Co(bzimpy)$_2$](ClO$_4$)$_2$ was characterized only by IR and UV/vis spectra [36]. Band at 9100 cm^{-1} was assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ transition.

Complexes with the ratio M:L 1:1 and 1:2 were also prepared with cobalt: (Co(bzimpy)X$_2$((X = Cl, Br, I), (Co(bzimpy)$_2$(X$_2$·2H$_2$O (X = Cl, Br, I) and (Co(bzimpy)$_2$((ClO$_4$)$_2$ [40]. All complexes are in the HS state (the measurement temperature was not given). Electronic spectra in the solid state (nujol suspensions) revealed distorted trigonal-bipyramidal geometry of the complexes (Co(bzimpy)X$_2$((X = Cl, Br). Complexes (Co(bzimpy)$_2$(X$_2$·2H$_2$O (X = Cl, Br, I) and (Co(bzimpy)$_2$OClO$_3$((ClO$_4$) form square bipyramids. However, it is not explained why one perchlorate group in the last complex is considered to coordinate to the central atom. When the ratio M:L 1:1 was used, anhydrous complexes were obtained whilst the hydrated complexes were obtained when the M:L ratio was 1:2.

The complexes (Co(bzimpy)Cl$_2$(and (Co(bzimpy)$_2$((ClO$_4$)$_2$ mentioned above were also investigated elsewhere together with the [Co(bzimpy)$_2$](SO$_4$)·H$_2$O, [Co(bzimpy)$_2$](NO$_3$)·H$_2$O and [Co(bzimpy$_{-\mathrm{H}}$)$_2$]·2H$_2$O [41]. Contrary to previous investigation [40] it was suggested that the complex (Co(bzimpy)Cl$_2$(is binuclear making use of the bridging property of chlorine atoms. Then each cobalt atom should be six-coordinate. Also coordination of the perchlorate group was suggested – even the splitting of its vibrations was observed in the IR spectra and was attributed to hydrogen bonds. Other counter anions, $NO_3{}^-$ and $SO_4{}^{2-}$, were not considered to be coordinated. The deprotonated ligand in the complex [Co(bzimpy$_{-\mathrm{H}}$)$_2$]·2H$_2$O was observed when Co(OAc)$_2$·4H$_2$O was used as a starting compound.

In [Co(bzimpy)Cl(MeOH)$_2$]Cl the coordination polyhedron around the cobalt atom can be viewed as a distorted octahedron [41]. The equatorial plane is formed by all three nitrogen atoms from the ligand and one chlorine atom. Axial positions are occupied by two oxygen atoms from methanol molecules. Also a system of hydrogen bonds was detected. Another coordination environment was detected in [Co(bzimpy)(MeOH)Cl]Cl·MeOH [149].

Another variation of coordination environment around the central cobalt atom was found for [Co(bzimpy)$_2$]Cl(OH)·3H$_2$O and [Co(bzimpy)Cl(H$_2$O)$_2$]Cl·2H$_2$O [150]. A complicated system of hydrogen bonding, involving acid imino hydrogen atoms of the ligand, water molecules as well OH^- and Cl^- groups, was discussed.

Binding in the cobalt(II) complex of *bzimpy* to DNA was investigated [103]. Similar results and the same problem can be observed in the case of the chromium(III) complex [85] (see d^3 systems). The reported complex [Co(bzimpy)$_2$] should be written as [Co(bzimpy$_{-\mathrm{H}}$)$_2$] as the authors have ignored the fact that one hydrogen atom is removed from each ligand molecule during complexation reaction. They concluded that the complex binds to DNA with moderate strength and the complex interacts with the DNA surface.

The complex (Co(bzimpy)$_2$((ClO$_4$)$_2$ was prepared by a microwave irradiation method. From electronic absorption and fluorescence spectra it follows that the complex can intercalate its benzimidazole moiety into the calf thymus DNA base pairs [57]. Catalytic activity of the complex [CoCl(bzimpy)$_2$]Cl·2H$_2$O was studied with respect to the oxidation of alcohols using O$_2$ and H$_2$O$_2$/O$_2$ as oxidants [49].

A magnetic moment of 4.78 B.M. suggests the presence of octahedral geometry with large orbital contribution in mixed ligand cobalt(II) complex [Co(bzimpy)$_2$(pa)$_2$] (pa = picric anion) [151]. Based on IR and UV/vis spectroscopy it was suggested that the ligand *bzimpy* is coordinated through only two nitrogen donor atoms whilst one nitrogen atom in the aromatic ring remains uncoordinated. Moreover, it was suggested that two picric molecules were coordinated either in *cis*- or *trans*-mode – the latter seems to be the more probable.

3.1.7. d^8 systems – Ni(II), Pd(II), Pt(II), Rh(I), Ir(I)

The complex (Ni(bzimpy)$_2$((ClO$_4$)$_2$·H$_2$O adopts an octahedral geometry with effective magnetic moment $\mu_{\mathrm{eff}}/\mu_{\mathrm{B}} = 3.22$ at 293 K. Electronic spectra are typical for octahedral Ni^{2+} complexes with the Racah parameters ($C = 4.709\,B$ and $B = 656\,\mathrm{cm}^{-1}$) [33,36]. The magnetic moment of the complex (Ni(bzimpy)$_2$((BPh$_4$)$_2$·H$_2$O is $\mu_{\mathrm{eff}}/\mu_{\mathrm{B}} = 3.35$ at 227 K [55]. The ligand was considered to be involved in a system of hydrogen bonds based on IR spectra.

It was suggested that the spin crossover in Fe(II) complexes could be expected when the Δ_0 value for the corresponding Ni(II) complex lay in the range 11,300–11,900 cm^{-1} [33]. The Δ_0 of interest spans the range where the energy levels of the Ni(II) complexes $^3T_{2g}(F)$ and $^1E_g(D)$ cross one another [33,152].

Complexes with the ratio M:L 1:1 and 1:2 were also prepared with nickel: (Ni(bzimpy)X$_2$((X = Cl, Br), (Ni(bzimpy)$_2$(X$_2$·H$_2$O (X = Cl, Br, I), (Ni(bzimpy)$_2$((ClO$_4$)$_2$ [40]. All complexes are in the HS state (the measurement temperature is not given). Electronic spectra in the solid state (nujol suspensions) revealed the complexes (Ni(bzimpy)X$_2$((X = Cl, Br) to form distorted trigonal bipyramids, complexes (Ni(bzimpy)$_2$(X$_2$·H$_2$O (X = Cl, Br, I) and (Ni(bzimpy)$_2$((ClO$_4$)$_2$ form octahedra. The formation of anhydrous or hydrated complexes depends on the ratio M:L analogously to the case of cobalt(II) complexes.

The ligand *bzimpy* in the structure of [Ni(ths)(bzimpy)(dmf)]·H$_2$O (ths = thiosulfate, dmf = dimethylformamide) coordinates in the usual mode through all three nitrogen donor atoms [153]. Two more coordination sites of the nickel are occupied by thiosulfate through the common S, O-chelate mode. The last coordination position is occupied by oxygen from dmf. Strong hydrogen-bonding interactions were observed whilst no π–π interaction between aromatic rings was observed.

Unusual coordination of the ligand *bzimpy* was found for the complex [Ni(NCS)$_2$(bzimpy)(H$_2$O)$_2$] [26]. Based on IR spectra it was concluded that the ligand *bzimpy* coordinates only through two nitrogen atoms. The equatorial plane is constructed from two nitrogen atoms of thyocyanato groups, one nitrogen atom from the ligand, and pyridine one, and one oxygen atom from a water molecule. Axial positions are occupied by one oxygen atom from a second water molecule and by one nitrogen atom from the ligand *bzimpy*, imidazole one. However, electronic transitions differ from those reported elsewhere [33,36,55].

For the complex [Ni(pa)$_2$(bzimpy)$_2$] (paH = picric acid) [27], based on IR spectra, it was concluded that paH acts as a monobasic mono-dentate ligand coordinating through the phenolic oxygen after deprotonation. The ligand *bzimpy* exhibits bidentate coordination, one donor site being the pyridine ring nitrogen, and the other the imidazole tertiary nitrogen. The composition of the complex suggests the possibility of *cis*- or *trans*-isomerization. However, the steric demand of the three nitro groups of the picric acid in the *cis*-structure makes the *trans*-structure more favourable. The described unusual behaviour of the ligand *bzimpy* can be emphasized by the fact that the studied complex is a bis-ligand one. Such behaviour was not observed for any other complex. These conclusions are not supported by any single crystal X-ray structural analysis for this complex and also not for its cobalt analogue.

In the structure of the complex $[Ni(N_3)(bzimpy)(MeOH)MeO]$ [154] the chromophore $\{NiN_4O_2\}$ adopts the shape of a pseudo-octahedron with the bond length of $Fe–N_{py}$ shorter than the bond lengths of $Fe–N_{bzim}$. Axial positions are occupied by two oxygen atoms while the equatorial plane is formed by four nitrogen atoms.

Palladium forms mononuclear complexes $[Pd(bzimpy)Cl_2]$ and $Pd(bzimpy)Br_2]$ as well as binuclear complex $[Pd_2(bzimpy)_3(ClO_4)](ClO_4)\cdot 2H_2O$ [155]. NMR investigation suggested both metal-to-ligand π back-donation and ligand-to-metal σ-donation. IR and NMR results suggest square planar coordination in all complexes in which even the ligand *bzimpy* possesses three potential donor atoms. In the complex $[Pd_2(bzimpy)_3(ClO_4)](ClO_4)\cdot 2H_2O$ two *bzimpy* ligands coordinate as chelating bidentate ligands whilst the third one is bridging bidentate. The binuclear nature of the complex was supported by FAB-mass spectroscopy exhibiting a molecular ion peak at $m/z = 1581$ as well as higher values indicating the formation of association fragments.

In the mononuclear complex $[Pd(cotl)(bzimpy)](ClO_4)$ (cotl = cyclooctenyl) ^1H- and ^{13}C-NMR spectra revealed that the N-heterocycles and the *cotl* group are coordinated to the metal ion. The results imply a relatively strong palladium-allyl bond [156]. The binuclear complexes $[\{PdX(cotl)\}_2(bzimpy)]$ (X = Cl or Br) seems to possess a pseudo four coordinate geometry around each metal ion. Here the *cotl* unit spans two adjacent coordination sites and the remaining two sites are coordinated by a halide ion and with the tertiary nitrogen of the benzimidazole unit.

The platinum(II) complex $[Pt(bzimpy)Cl](PF_6)$ emits weakly from its MLCT state and this was investigated with a view to the connection of metal-based sensors for biological applications such as molecular light switches. This complex binds to the hydrophobic pockets of bovine serum albumin [44].

Complex $[Rh(CO)_2(bzimpy)]Cl\cdot 1.5H_2O$ exhibits interesting catalytic activity [49]. It reversibly binds CO and in alcoholic solvents loses CO. When NO or O_2 is passed through a 2-methoxy ethanolic solution of the complex carbon dioxide is formed. A catalytic cycle for the reduction of NO and O_2 was suggested.

For comments on $RhX(CO)_2(bzimpy)\cdot 1.5H_2O$ (X = Cl, Br), $RhX(bzimpy)\cdot 2H_2O$, $Rh(bzimpy)(CO)(OClO_3)$ and $IrX(CO)_2(bzimpy)\cdot nH_2O$ (X = Cl, $n = 1$; X = Br, $n = 1.5$) complexes see d^6 system [23].

3.1.8. d^9 systems – Cu(II)

A central atom of Cu(II) forms complexes with *bzimpy* in the ratio M:L = 1:1 and 1:2 of the following compositions: $(Cu(bzimpy)NCMe(ClO_4)_2($, $[Cu(bzimpy)(ClO_4)_2]\cdot 2H_2O$, $(Cu(bzimpy)_2((ClO_4)_2$, $Cu(bzimpy)(NO_3)_2\cdot 2H_2O$, $[Cu(bzimpy)Cl_2]\cdot 2H_2O$, $[Cu(bzimpy)Br_2]\cdot 0.5H_2O$ [157]. X-ray analysis showed that in the complex $(Cu(bzimpy)NCMe(ClO_4)_2($ the central atom is coordinated by three nitrogen atoms from the ligand and by one nitrogen atom from acetonitrile in the equatorial plane. Axial positions are occupied by oxygen atoms from perchlorate groups but one is situated at a longer distance; thus one can speak of semi-coordination (Cu–O(1) 2.396(2) Å, Cu–O(2) 2.817(3) Å). The plane of four nitrogen atoms forms an almost perfect square. Also two hydrogen bonds are present between N–H of the benzimidazole group and an oxygen atom from the perchlorate group. For copper complexes with the composition M:L = 1:2 it is supposed that the tridentate ligand *bzimpy* cannot coordinate to the central atom in an octahedral manner (one ligand is coordinated by three donor atoms and the second ligand by two donor atoms) because of small ionic radius relative to other central atoms. The Jahn-Teller effect is operative here [157]. Electronic and EPR spectra of 1:1 complexes revealed that coordination polyhedra contain three nitrogen atoms from the ligand and two donor atoms from the counter-anion or solvent molecules. These atoms form a square pyramid and the sixth atom can be coordinated in the second axial position but at higher distance [157]. For the complex $[Cu(bzimpy)NCMe)](ClO_4)_2$ an irreversible Cu(II)/Cu(I) redox process was observed [158], see also [157].

The copper(II) complex [Cu(bzimpy)Cl]Cl shows no deprotonation of the ligand [159], contrary to cobalt(II) [103] and chromium(III) [85] complexes. The complex binds to DNA moderately through an intercalative mode.

The complex $[Cu(bzimpy)](ClO_4)_2\cdot 3H_2O$ was studied in terms of solution chemistry [160]. In solution the EPR and UV/vis spectra are consistent with tetragonal structure. Addition of OH^- to the solution results in a double deprotonation of the ligand prior to substitution of the coordinated aprotic solvent with OH^- that takes place in the third step.

The complex $[Cu(bzimpy)Cl_2]\cdot DMF$ adopts square-pyramidal geometry with the equatorial plane formed from all three nitrogen atoms of the ligand and one chlorine atom [160,161]. A non-coordinated molecule of DMF is involved in the hydrogen bonding network. Also a bis-ligand complex of the composition $[Cu(bzimpy)_2]Cl_2\cdot EtOH\cdot H_2O$ was reported [60].

Complexes of the ligand *bzimpy* with different copper(II) salts in DMF solution were also investigated by fluorescent spectroscopy [162]. Such a complex could be used as a sensor for the detection of soft acid metal ions. Only Cu(II) ions can quench the fluorescence of the ligand *bzimpy*.

In the complex $(Cu(bzimpy)(H_2O)_2(ONO_2)((NO_3)\cdot H_2O$ the chromophore $\{CuN_3OO'O''\}$ contains an equatorial plane formed by three nitrogen atoms from the ligand and by an oxygen atom from the water molecule. Axial positions are occupied by oxygen atoms from the second water molecule and from a NO_3^- group but in significantly different distances. EPR spectra showed three peaks. When exchange interactions among differently orientated chromophores were taken into account a set of $g_{||}$ and $g_{\perp}$ values were obtained corresponding to the chromophore $\{CuN_3O_3\}$ of the elongated square-bipyramidal geometry 4 + 1 + 1 [163].

The binding of molecular oxygen to the central copper atom was observed in the complex $[Cu(bzimpy)Cl(H_2O)O_2]Cl$ [164]. The complex binds to bovine serum albumin through two specific binding sites.

In mixed valence binuclear copper(II)-copper(I) complexes of the composition $[(bzimpy)\text{-}Cu\text{-}\mu Cl_2\text{-}Cu\text{-}X]$ (X = Cl, I, SCN) [165] Cu(II) and Cu(I) atoms are bridged by two chlorine atoms. Mixed valence complexes show room temperature magnetic moments in the range 1.79–1.81 B.M. EPR spectroscopy revealed a larger separation in g_x and g_y in complexes with X = Cl and I than in the monovalent complex $[(bzimpy)CuCl_2]$.

The complex $[Cu(bzimpy)(ClO_4)Cl]\cdot H_2O$ contain both perchlorate and chlorine ligands coordinated to the central atom [166]. The coordination geometry around the copper atom is best described as distorted square pyramid with three nitrogen atoms of the ligand *bzimpy* and a chlorine ion defining the equatorial plane. The apical position is occupied by an oxygen atom from the perchlorate group. The water molecule, which is a better donor than the perchlorate group, remains uncoordinated. The molecular structure exhibits different hydrogen bonds of the type N–H. . .O, O–H. . .O and O–H. . .Cl. Electronic and EPR spectra indicate square pyramidal geometry around the copper atom with axial elongation.

A copper(II) complex with the twofold deprotonated form of the ligand *bzimpy* of the following composition $Cu(bzimpy_{-2H})\cdot 0.75EtOH$ was suggested, but not characterized [60].

3.1.9. d^{10} systems – Zn(II), Cu(I), Cd(II), Hg(II) In(III), Pb(II), Ag(I)

A central atom of Zn(II) forms complexes with *bzimpy* in the ratio M:L = 1:1 of the following composition: [Zn(bzimpy)Cl_2]·nH_2O (n = 2 [157], n = 0 [59]), [Zn(bzimpy)Br_2]·H_2O [157]. Based on IR spectra it was concluded that Zn–Cl bonds are terminal. Moreover, this complex shows strong antimicrobial activity.

The formation of a monoligand chloride complex was proven by the structure of the complex [Zn(bzimpy)Cl_2]·DMF [167]. The zinc(II) cation shows distorted trigonal-bipyramidal coordination by three N atoms and two Cl atoms. N–H...O and N–H...Cl hydrogen bonds were identified together with interplanar distances in the range 3.4–3.6 Å, indicating a π–π stacking interaction between adjacent molecules. Independently the structure of the same complex was described by [168] with comparable results although different space groups were suggested. Single crystals analysed by [168] were prepared by recrystallization of [Zn(bzimpy)Cl_2]·MeOH. This complex shows an emission peak at 555 nm, electroluminescent efficiency 0.017 cd A^{-1} and turn-on voltage 7 V, compared to 470 nm, 0.036 cd A^{-1} and 9 V for the ligand. Finally, the complex is capable of functioning as a blue emitter in electroluminescent devices.

The monoligand complex [Zn(bzimpy)NO_3](NO_3) was studied by UV/vis, pH dependent ^1H NMR and IR spectroscopies. The complex binds to DNA base pairs via the ligand [169]. The viscosity of DNA decreases as complex concentration increases. The complex [Zn$(bzimpy)_2$]$(ClO_4)_2$ was characterized by IR and UV/vis spectra [36]. Contradictory results were presented in [39]. Based on IR spectra it was suggested that one perchlorate group is coordinated to the central atom thus the complex should read as [Zn$(bzimpy)_2$(ClO_4)](ClO_4) when the coordination polyhedron adopts square-pyramidal geometry and this was confirmed by measurements of electrical conductivity giving the results for a 1:1 electrolyte. This implies that both ligands should coordinate through only two nitrogen atoms. However, steric conditions, excluding the coordination of any other group than two *bzimpy* ligands, are in contradiction to the above observation.

The acidity of the imino-hydrogen of the ligand *bzimpy* in [Zn$(bzimpy)_2$]$(ClO_4)_2$·$2H_2O$ increases on coordination to the zinc(II) ion. For the protonation reaction the following values were established ΔH = 123.55 kJ/mol and ΔS = 143.30 J/K mol [170]. The complex [Zn$(bzimpy)_2$]$(ClO_4)_2$·$3H_2O$ was characterized only by UV/vis spectra in acetonitrile solution [80].

The central atom in coordination polymer of composition [Zn(bzimpy)(p-CPOA)]$_n$ (p-CPOA = p-carboxylacetate dianion) is penta-coordinated, surrounded by two carboxylate oxygen atoms from two different p-CPOA groups in a bis-monodentate mode and three nitrogen atoms from *bzimpy* forming a distorted trigonal bipyramid [171]. Each pair of adjacent Zn(II) atoms are bridged by p-CPOA ligands forming a chiral helical chain. The adjacent helices are packed through hydrogen bonds and π–π interaction was also identified.

The Zn(II) atom in analogous polymer [Zn(bzimpy)(p-pdoa)]$_n$ (p-pdoa = p-phenylenedioxydiacetate) assumes a distorted trigonal bipyramidal geometry, involving two carboxyl O atoms from two different p-pdoa ligands and three N atoms from the *bzimpy* ligand [172]. There exists a 2D framework linked by π–π stacking (3.312 Å) between adjacent benzimidazoles of *bzimpy* ligands and there also exist two interlayer π–π stacking interactions of 3.299 Å between adjacent central pyridines of the *bzimpy* ligand and 3.176 Å between the Ph groups of the p-pdoa ligand. Such π–π stacking interactions extend the two-dimensional layers into a 3D supramolecular network.

A mixed ligand complex of the composition [Zn(bzimpy)TDT] (TDT = 3,4-toluenedithiolate) was suggested to belong to the category of complexes in which the ligand *bzimpy* coordinates through only two nitrogen atoms, whilst the last one remains uncoordinated [173]. Ligand-to-ligand charge transfer behaviour was identified based on UV/vis spectra.

Two singly deprotonated ligands in [Zn$(bzimpy_{-H})_2$]coordinate to the central atom in the expected fashion making “crosses” [42]. It was suggested that the position of the only acid hydrogen atom is disordered. One hydrogen interaction was observed although coordination geometry does not allow any kind of π interaction. The same compound was also reported by [43] but with completely different crystallographic data including cell parameters. This discrepancy has no reasonable explanation. Moreover, a significant uncertainty is introduced into the explanation of protonated and hydrogen free nitrogen atoms. In the latter report blue-fluorescent emission was identified.

The following complexes of cadmium(II) [Cd($bzimpy_{-H}$)(bzimpy)]X (X = ClO_4, BF_4), [Cd($bzimpy_{-H}$)(OAc)], [Cd$(bzimpy_{-H})_2$], [Cd(bzimpy)Cl_2]·H_2O and [Cd(bzimpy)$(NO_3)_2$]·0.5H_2O [174] were prepared and characterized by IR and NMR spectra (as well as free ligand) and electrical conductivity. In the complex [Cd(bzimpy)Cl_2]·H_2O chlorine atoms are coordinated to the central atom that is five-coordinated. Similar results arose from an investigation of the water free complexes [Cd(bzimpy)Cl_2] [59] and [Cd(bzimpy)Cl_2]·DMF [175], the last one emitting blue luminescence in the solid state and in DMF solution. In the nitrate complex one NO_3 group is coordinated in bidentate manner whilst the second one is uncoordinated. Thus the central atom is again five-coordinated. In the acetate complex the acetate group is also coordinated. In all other complexes two ligand molecules are present so it is most likely that the central atom is six-coordinated. The coordination polyhedron of the complex [Cd$(bzimpy_{-H})_2$] adopts pseudo-octahedral geometry. Hydrogen bonds were also observed. It was stated that no π-stacking was observed but this observation was considered only for the complex itself. The last compound was also reported by [43]. Analogously to the case of the zinc(II) complex, uncertainty in the explanation of protonated and hydrogen free nitrogen atoms remains. Blue-fluorescent emission was identified with bathochromic shift of the emission energy in contrast to the free ligand.

The tendency to form monoligand complexes with cadmium was also confirmed in the case of the perchlorate complex of composition [Cd(bzimpy)(ClO_4)](ClO_4). Based on IR spectra the coordinating mode of the perchlorate group was identified and in combination with electric conductivity measurements it was concluded that only one perchlorate group coordinates to the central atom thus possessing tetrahedral coordination [39].

In the mixed ligand polymeric complex of composition [Cd(bzimpy)(p-PDOA)]$_n$ (p-PDOA = p-phenylenedioxydiacetate dianion) the central cadmium(II) atom is coordinated by seven donor atoms; three nitrogen atoms from the ligand *bzimpy* and four oxygen atoms from p-PDOA, adopting distorted pentagonal bipyramid geometry [176]. The shortest Cd···Cd interaction is 11.4 Å and the face-to-face distance of two *bzimpy* ligands is 3.5 Å that corresponds to moderate π–π interaction. The compound is stable up to 389 °C. Blue fluorescent emission of this complex was determined at 428 nm with a decay lifetime of 7.24 ns.

The compound $Cd_2(bzimpy)_2(Ac)_3$·$0.5S_2O_8$·$2H_2O$ is binuclear with two independent Cd atoms per asymmetric unit, two *bzimpy* ligands and three acetate groups; one monodentate, another bidentate and the third bidentate ligand acting as a bridge between both metals [177]. An unusual *cis* conformation of *bzimpy* leading to a clear intramolecular π–π interaction together with a complex hydrogen bonding scheme is present.

The [Hg(bzimpy)Cl_2]·complex was investigated by IR, NMR and UV/vis spectroscopy [59] – the results correspond to those for the analogous Zn(II) and Cd(II) complexes.

In the structure of the complex [Hg(bzimpy)Cl_2]·2DMF the central atom is five coordinated and adopts a distorted trigonal-bipyramidal geometry [63]. Intermolecular π–π interaction was identified in the solid state with the distance 3.42 Å. This intermolecular π–π interaction suggests a charge transport property of the complex, which is an essential property of electroluminescent material. Luminescent emission of the complex is red shifted in comparison with free ligand that has a blue emission band at 374 nm.

The complex $[Hg(bzimpy)(ClO_4)](ClO_4)$ [39] has similar properties to its cadmium analogue.

The silver (I) complex $[Ag(bzimpy)](ClO_4)$ exhibits unsplit perchlorate vibrations in the IR spectra, that indicates that perchlorate anions are not coordinated [178].

The complex $[In(bzimpy_{-H})Cl_2(H_2O)]\cdot DMF$ contains the ligand in anionic form and emits blue luminescence in the solid state and in DMF solution [175].

In the case of the Pb(II) complex $[Pb(bzimpy)(H_2O)_2(NO_3)_2]\cdot bzimpy\cdot H_2O$ [179] each lead atom is chelated by the nitrogen atoms of the *bzimpy* ligand and by the oxygen atoms of nitrate anions and also by the oxygen atoms of two water molecules. The arrangement of *bzimpy*, water and nitrate ligands suggests a gap or hole in coordination geometry around the metal ion. There is one molecule of *bzimpy* and one water molecule that are not coordinated to the lead atom. A significant network of hydrogen interactions was observed.

3.1.10. f^x systems

The study of the luminescence spectra of lanthanides, especially Eu^{3+}, is important from the biological point of view, because Eu^{3+} has similar physico-chemical properties to those of (biologically active) Ca^{2+}. This research was carried out on the complexes $(Ln(bzimpy)_2(NO_3)_2((NO_3)\cdot n MeOH$ (Ln = Ce n = 0, 3, Ln = Eu, Tb n = 0, 2) that were characterized by single crystal X-ray diffraction (only complexes with crystal methanol), IR and NMR spectroscopy and conductivity measurements [180]. All three complexes with crystal methanol are ten-coordinated (forming sphenocorona or tetradecahedron for the Ce complex and distorted bicapped square antiprism for Eu and Tb complexes) with six nitrogen atoms from both ligands and four oxygen atoms from two coordinated nitrate groups in bis-functional manner and hydrogen contacts were observed. The complex $(Sm(bzimpy)_2(NO_3)_2((NO_3)$ was also prepared [180]. Luminescence properties of all these complexes were investigated because of their potential industrial applications.

The lanthanide complexes can be also prepared as by-product of a template synthesis, [54] when a lanthanide salt reacts with 1,2-diaminobenzene and 2,6-pyridinedicarboxylaldehyde.

Other complexes with different amounts of crystal water were prepared $[Ln(bzimpy)_2(NO_3)_2](NO_3)\cdot H_2O$ (Ln = La, Ce, Nd, Pr, Eu, Gd, Tb), $[Sm(bzimpy)_2(NO_3)_2](NO_3)\cdot 2H_2O$ as well as other complexes with deprotonated ligand $[Dy(bzimpy)(bzimpy_{-H})(NO_3)(OH_2)](NO_3)\cdot 4H_2O$, $[Er(bzimpy)(bzimpy_{-H})(NO_3)(OH_2)](NO_3)\cdot 3H_2O$, $[Lu(bzimpy_{-H})(NO_3)_2(OH_2)]\cdot 2H_2O$ [181]. All of them were characterized by IR and UV/vis spectra, molar conductivity, thermal analysis and X-ray powder diffraction patterns, any structure was given. Again, the complexes of Dy(III), Er(III) and Lu(III) with deprotonated ligands were formed unexpectedly without addition of any base. Only a general procedure of complex preparation was given and it is not clear why two different products were obtained. Ce and Eu complexes are isomorphous. In all complexes luminescence of ligand was observed while in the case of Sm, Eu and Tb complexes the metal ion luminescence was observed as well.

In the complex $[Lu(bzimpy_{-H})(NO_3)_2(MeOH)_2]\cdot(bzimpy)\cdot 2MeOH$ the central lutetium atom is nine-coordinated by three nitrogen atoms from deprotonated ligand, by four oxygen atoms from two bidentate NO_3 groups and by two oxygen atoms from two methanol molecules [25]. The polyhedron adopts the distorted tricapped trigonal prismatic geometry. The coordinated ligand spontaneously deprotonates during complex preparation without addition of any base (this was observed in several other cases (see above)). This is the another example in which the second ligand is not directly coordinated to the central atom, but is bound in the structure via a complicated hydrogen bond network (see complex of lead). Contrary to the case of transition metal complexes the bond Lu-N_{bzim} is longer than Lu-N_{py}.

Soft X-ray scanning transmission X-ray spectromicroscopy was successfully utilized to collect NEXAFS spectra from the uranium(IV) actinide complex $[U(bzimpy)_3Cl_4]\cdot x THF$ [182] with the aim of understanding ^{5}f electron behaviour in actinide complexes.

3.2. Complexes of the ligand 2,6-bis-(benzthiazol-2-yl)-pyridine

With the ligand 2,6-bis-(benzthiazol-2-yl)-pyridine (*bztpy*) both, mono-ligand and bis-ligand complexes were prepared. Mono-ligand complexes of the general formula $Fe(bztpy)X_2$ can be five coordinated monomers or six coordinated bridged dimers. To distinguish between them Mössbauer spectroscopy is helpful [80].

The ligand *bztpy* can act as a tridentate ligand but it can also act as a monodentate or bidentate ligand. The pyridine nitrogen atom is a stronger base than the benzthiazole nitrogen atoms. Thus, its zinc or mercury complexes could be most likely tetrahedral with bidentate functionality of the ligand. In such complexes, the ligand is coordinated to the central atom via the pyridine nitrogen atom and one benzthiazole nitrogen atom [183].

A complete survey of the complexes with the ligand *bztpy* is in Table A4 in Appendix B.

3.2.1. d^5 systems – Mn(II), Fe(III), Ru(III)

The central Mn(II) atom in the complex $[Mn(bztpy)Cl_2]\cdot 1/2H_2O$ can be six or five coordinated [72]. Based, as it was, on only spectral investigation this was not differentiated. The complex $[Mn(bztpy)(ClO_4)_2]$ is high spin with ground state ^{6}A [28].

The ligand *bztpy* in the complexes $[Fe(bztpy)_2]Cl_3\cdot H_2O$ and $[Ru(bztpy)Cl_3]\cdot EtOH$ could behave as tridentate [183]. The complex $(Fe(bztpy)Cl_3(\cdot x H_2O$ (starting with an Fe(II) salt) is high-spin at 77 K [80]. The structure of only two metal complexes with *bztpy* was described in the literature; complexes $[Fe(bztpy)Cl_3]\cdot CHCl_3$ and $[Fe(bztpy)Cl_3]\cdot MeNO_2$ [28]. In the complex $[Fe(bztpy)Cl_3]\cdot CHCl_3$ a ratio M:L 1:1 was obtained in spite of a starting experimental ratio of 1:2 [28] whilst in the case of $[Fe(bztpy)_2]Cl_3\cdot H_2O$ a ratio of 1:2 was obtained in spite of a starting ratio of 1:1 [183]. In the last case the starting salt was $FeCl_3\cdot 6H_2O$ whilst in the previous one anhydrous $FeCl_3$ was used.

In the structure of both complexes, $[Fe(bztpy)Cl_3]\cdot CHCl_3$ and $[Fe(bztpy)Cl_3]\cdot MeNO_2$, the ligand *bztpy* adopts the *cis*-N_{bzt}-N_{py}-N_{bzt}, configuration contrary to the pure or protonated form of the ligand with *cis*-S_{bzt}-N_{py}-S_{bzt} configuration. This indicates a complicated reaction mechanism of complexation. Moreover, the presence of different crystal solvent molecules results in different arrangements of the ligand molecules in the crystal structure and in different cell parameters. In the complex $[Fe(bztpy)Cl_3]\cdot CHCl_3$ the ligands are arranged in puckered planes in a similar manner to that in the pure or protonated form of *bztpy* and $(bzimpyH)(ClO_4)\cdot H_2O$; in $[Fe(bztpy)Cl_3]\cdot MeNO_2$, the ligands, however, are situated in two mutually perpendicular planes (Fig. 20). In both cases, the molecular cation is hexa-coordinated with the $\{FeN_3Cl_3\}$ chromophore. This means that the central iron atom is coordinated by all three nitrogen atoms from the ligand and the octahedral coordination is completed by three chloro-ligands. A similar dependence of cell parameters on the presence of crystal solvent molecules was observed in the series of complexes $[Fe(2\text{-}pic)_3]Cl_2\cdot sol$ (2-pic = 2-

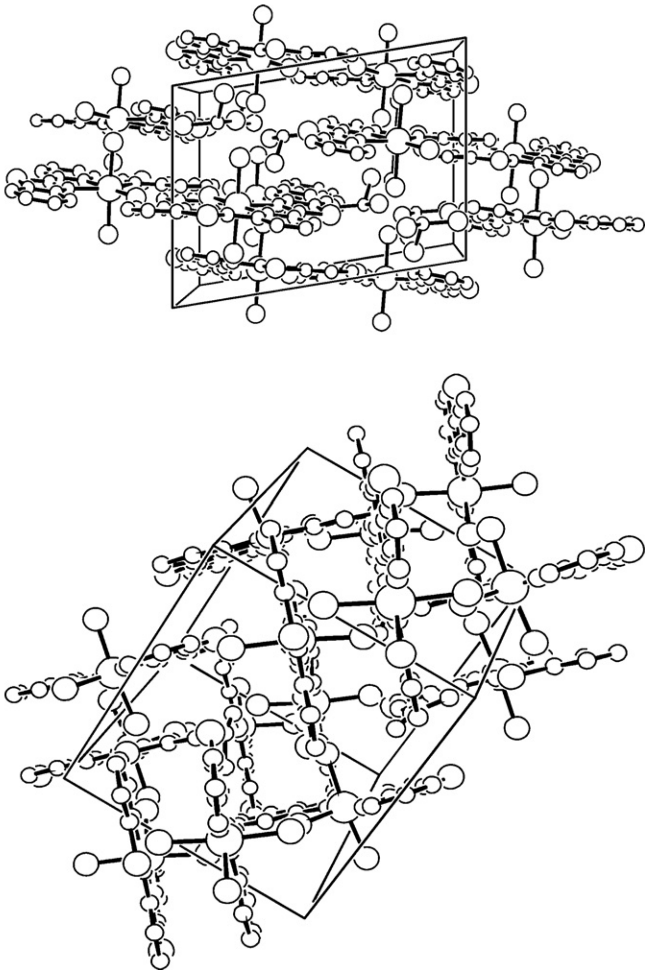


Fig. 20. PLUTO pictures of the unit cell content for $[Fe(bztpy)Cl_3]{\cdot}CHCl_3$ (top) and $[Fe(bztpy)Cl_3]{\cdot}MeNO_2$, (bottom). According to [28] with kind permission from the publisher.

(aminomethyl)pyridine), where sol was EtOH (P 21/c), MeOH (P bca), $2H_2O$ (P 1) and H_2O (–) [184].

Magnetic properties of the following compounds $[Fe(bztpy)(NO_3)_3]{\cdot}1.5CHCl_3{\cdot}MeOH$, $[Fe(bztpy)_2](ClO_4)_3{\cdot}2CHCl_3{\cdot}H_2O$, $[Fe(bztpy)_2](ClO_4)_3{\cdot}CHCl_3{\cdot}3H_2O$ $[Fe(bztpy)_2](ClO_4)_3{\cdot}2CHCl_3{\cdot}3H_2O$ and $[Fe(bztpy)_2(BF_4)_3]$ are very sensitive to their composition [28]. Perchlorate Fe(III) complexes show much higher variability of magnetic behaviour. They can be low-spin with the ^2T state or intermediate spin with the ^4T state, depending upon the ratio of co-crystallized chloroform and water molecules.

The intermediate state for the low-symmetry Fe(III) chromophores is nothing rare. The hypothesis of the intermediate ^4T state for the complex $[Fe(bztpy)_2](ClO_4)_3{\cdot}2CHCl_3{\cdot}H_2O$ has been confirmed by a good fit of magnetic data: with fixed $\lambda^{sf}/hc = +153\,cm^{-1}$ and $g_1 = -1.5$ the value of $\Delta_{ax}/hc = 213\,cm^{-1}$ resulted [28]. The comparison of variation of magnetic properties is shown in Fig. 21.

For the complex $[Fe(bztpy)_2](ClO_4)_3{\cdot}2CHCl_3{\cdot}3H_2O$ the Mössbauer spectra were recorded at $T = 4.2$ K and $T = 295$ K. The sample contains several magnetically non-equivalent centres all being in the low-spin state at low temperature. Only one of these centres alters its low-spin state to the high-spin one on passing to room temperature [28].

The complex $[Fe(bztpy)_2](NO_3)_3{\cdot}2.5CHCl_3$ was also prepared but was not satisfactorily characterized [60]. By variation of experimental conditions different solvent can be incorporated and even a different metal to ligand ratio can be achieved.

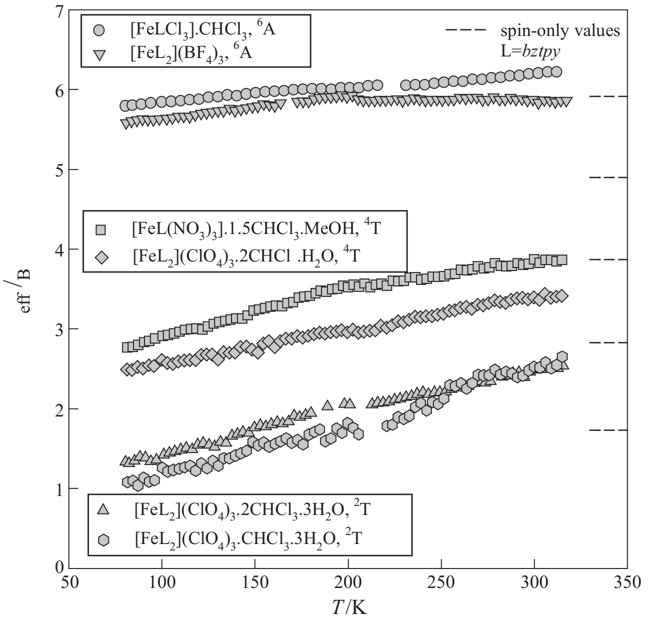


Fig. 21. Temperature variation of the effective magnetic moment for Fe(III) complexes of *bztpy*. Ground states are indicated. According to [28] with kind permission from the publisher.

3.2.2. d^6 systems – Fe(II), Ru(II), Rh(III)

The mono-ligand complexes $[Fe(bztpy)X_2]{\cdot}nH_2O$ (X = Cl, NCS, $n = 1/2$; X = Br, I, $n = 0$) seems to be five coordinated based on spectral data [72]. The complex $(Fe(bztpy)Cl_2({\cdot}2H_2O$ is high-spin at 77 K [80].

Complexes $[Fe(bztpy)I_2]$, $(Fe(bztpy)(NCS)_2({\cdot}1/2H_2O$ and $[Fe(bztpy)_2(Br(FeBr_4($ were high spin at 300 K with a large value of quadrupolar splitting [185].

In the bis-ligand complexes $[Fe(bztpy)_2](ClO_4)_2{\cdot}3H_2O$ and $[Fe(bztpy)_2(Br(FeBr_4($ the temperature dependence of magnetic moment was followed, pronounced in the perchlorate complex [72]. The spin crossover behaviour of the complex $(Fe(bztpy)_2((ClO_4)_2{\cdot}3H_2O$ was confirmed by Mössbauer spectroscopy [185]. For the complex $(Fe(bztpy)_2((ClO_4)_2{\cdot}CHCl_3$ a more complete conversion of the LS to HS states was observed at higher temperatures [29] relative to the above complex $(Fe(bztpy)_2((ClO_4)_2{\cdot}3H_2O$ [72].

The magnetic behaviour of the complexes $(Fe(bztpy)_2((ClO_4)_2{\cdot}S$ (S = $4H_2O$, $3H_2O$, $0.75CHCl_3$) appears to be strongly dependent on the manner of preparation. According to some literature data [80] all these complexes are high-spin but according to [29] the complex $(Fe(bztpy)_2((ClO_4)_2{\cdot}3H_2O$ exhibits spin crossover with values of the magnetic moment ranging between 4.49 μ_B at 313 K and 2.23 μ_B at 83 K. Pure high-spin or low-spin samples over the whole measured temperature range of 77–295 K were prepared for the complex with S = $4H_2O$ [80].

Other Fe(II) perchlorate complexes with were prepared containing different crystal solvent molecules: $[Fe(bztpy)(phen)](ClO_4)_2{\cdot}CHCl_3$, $[Fe(bztpy)_2](BPh_4)_2{\cdot}2CHCl_3$ and $[Fe(bztpy)(NO_3)_2]$ [28]. For the Fe(II) complex $[Fe(bztpy)(phen)](ClO_4)_2{\cdot}CHCl_3$ some features of the spin transition were observed. The effective magnetic moment shows a step at $T = 170$ K and then a gradual increase. A transition from a ^1A state to the intermediate spin state ^3A could exist along with the lowered symmetry of the chromophore. The g-factor of the intermediate-spin state was $g_{eff} = 2.51$ and the spin crossover parameters were $(\Delta_0/k) = 1063$ K and $r_{\mathrm{eff}} = 206$. With these data the transition temperature $T_c = \Delta H/\Delta S = N_A\Delta_0/(R \ln r_{\mathrm{eff}}) = 200$ K matching well the step in the effective magnetic moment. The remaining two complexes are high-spin with magnetic moments higher than the spin only value.

Unexpectedly, a monoligand perchlorate complex was also prepared (Fe(bztpy)$(ClO_4)_2$([60].

The complex [Ru(bztpy)$_2$]Cl_2 (from [Ru(bztpy)Cl_3 as a precursor]) was synthesized [102] as a model compound for Ru(II) polymer complexes. This polymer consists of ligands *bztpy* connected through the position 5- on the benzene ring. After complexation of the polymeric ligand the photosensitivity was enhanced whilst no electroluminescence was found in the polymeric complex.

The ligand in the complex [Rh(bztpy)Cl_3]·$2H_2O$ could behave as tridentate [183]. The complex [Ru(bztpy)$_2$]$(PF_6)_2$·DMF was also synthesized [186], but because of its low solubility it was not characterized by any solution-based measurements.

3.2.3. *d^7 systems – Co(II)*

The values of the effective magnetic moment for the bis-ligand Co(II) complexes (Co(bztpy)$_2$(($ClO_4)_2$·$5H_2O$, [Co(bztpy)$_2$(($BF_4)_2$·$4H_2O$ (4.66–4.83 μ_B) indicate the existence of six coordinated high-spin complexes. Magnetic moments of the mono-ligand Co(II) complexes (Co(bztpy)X_2(·nH_2O (X = Cl, $n = 1/2$; X = Br, NCS, $n = 0$) are lower (4.42–4.54 μ_B) and were reported as five coordinated with tridentate functionality of the ligand [72]. The electronic spectra of the bis-ligand Co(II) complexes show two weak bands at 8500–12,000 cm^{-1} and a shoulder at 20,000 cm^{-1}. These values are characteristic of high-spin octahedral complexes. Mono-ligand Co(II) complexes are five coordinated according the UV/vis spectra except for the complex (Co(bztpy)$(NO_3)_2$(that seems to be octahedral [72]. In the infrared spectra of the latter complexes, bands at 1022 cm^{-1} and 1011 cm^{-1} occurred; these belong to a NO_3^- vibration. Moreover, in the region 1500–1250 cm^{-1} four additional peaks belonging to NO_3^- vibration appear. Such an increase of the number of vibrations together with their position indicates the presence of both, mono- and bidentate nitrate groups. The lowering of the symmetry of the complex may cause a similar effect [72].

The ligand *bztpy* in the complex [Co(bztpy)I_2] could behave as either bidentate or tridentate [183]. The Co(II) complex [Co(bztpy)$_2$]$(CF_3SO_3)_2$·$CHCl_3$ is high-spin; its effective magnetic moment is higher than the spin-only value for $S = 3/2$ (3.87 μ_B) and increases gradually with temperature [28]. Two more complexes were prepared but were not characterized [Co(bztpy)$(PF_6)_2$]·$4H_2O$ and [Co(bztpy)$_2$]$(BF_4)_2$·$CHCl_3$ [60]). Slight changes of the counter-anion employed can result in the formation of either a mono- or a bis-ligand complex.

3.2.4. *d^8 systems – Ni(II), Pd(II)*

Based on electronic spectra the complexes (Ni(bztpy)X_2((X = Cl, NO_3) were identified as octahedral. In this case one can suppose a bridging behaviour of the counter-anions. Following the infrared and electronic spectra one can suppose the complex (Ni(bztpy)Cl_2(to be polymeric with chloro-bridges, whereas the complex (Ni(bztpy)$(NO_3)_2$(can form a polymeric structure with one bridging nitrate group, or it can form a monomeric structure with one mono-dentate and one bi-dentate nitrate group [72]. The ligand in the complex [Ni(bztpy)$_2$]$(ClO_4)_2$·$2H_2O$ possibly behaves as tridentate [183].

The Ni(II) complex [Ni(bztpy)$_2$]$(ClO_4)_2$·$CHCl_3$ shows a gradual increase of the effective magnetic moment with temperature. Its value (3.2–3.9) is higher than the spin-only value. Thus the term $^3T_1$ of a tetrahedral geometry is to be considered instead of the $^3A_{2g}$ term for an octahedral coordination [28]. In the complex (Pd_2(bztpy)Cl_4(the presence of Pd–$(Cl)_2$–Pd bridges is expected [183] and fragment $PdCl_2PdCl_2$ is coordinated through nitrogen atoms of benzthiazole groups.

3.2.5. *d^9 systems – Cu(II)*

The ligand in the complex [Cu(bztpy)Br_2] could behave as bidentate or tridentate whilst in the complex [Cu(bztpy)Cl_2]·H_2O it behaves as tridentate [183]. Complexes [Cu(bztpy)]$(ClO_4)_2$ and [Cu(bztpy)Cl](ClO_4) were studied in solution by EPR and UV/vis spectra showing the [Cu(bztpy)]$^{2+}$ to have tetragonal structure with the fourth coordination site occupied by solvent [160].

3.2.6. *d^{10} systems – Zn(II), Hg(II), Ag(I)*

It was suggested that in the complexes [Zn(bztpy)Cl_2], [Hg(bztpy)Cl_2] and [Hg(bztpy)Br_2] the potentially tridentate ligand coordinates to the central atom via only two nitrogen atoms; one pyridine and one benzthiazole nitrogen atom forming a tetrahedral environment around the central atoms [183].

A complex (Zn(bztpy)$_2$(($ClO_4)_2$·$3H_2O$ was prepared and characterized by only UV/vis spectra [80]. Different hydrates of some zinc(II) complexes were also prepared – Zn(bztpy)X_2·nH_2O ($n = 1$, X = Cl; $n = 0$, X = Br, I) and (Zn(bztpy)$_2$(H_2O)(($ClO_4)_2$·H_2O [187]. An attempt to obtain the structure of these complexes was done based on molar conductivity measurements, TGA analysis IR and ^{1}H NMR spectra. The interesting suggestion is that for the perchlorate complex one ligand behaves as tridentate whilst the second one is bidentate enabling the coordination of a water molecule in the remaining sixth position. The complex [Ag(bztpy)(ClO_4)] was prepared but not characterized [183].

4. Some comparison, comments and concluding remarks

As was noted in the Introduction, the coordination behaviour of the ligands *bzimpy* and *bztpy* is significantly more variable as one could expect taking into account the rigidity of these ligands. The ligand *bzimpy* is a planar molecule with a rotation barrier (around a C–C bond) of ca. 225 kJ mol^{-1}. Such rigidity has roots in π delocalization [163]. Even this value seems to be significantly higher compared with biphenyl (<15 kJ mol^{-1}) it can be lowered by steric hindrance of various origin (hydrogen bonding, co-crystallizing building fragments, etc.). A very simple comparison arising from structural data is found in Table S1 in supplementary materials in which a summary of bond distances of the first coordination sphere of all structurally studied complexes is given. In principal, the bond distances between the central atom and the pyridine nitrogen atoms are shorter than those between the central atom and the imino-nitrogen atoms from the benzimidazole rings. More than forty structures with the ligand *bzimpy* were solved but only two structures with the ligand *bztpy*. This indicates that some gaps in the structural investigation of the benzthiazole analogues exist. The distances M–N_{py} and M–N_{bzim} largely follow the order Mn > Co > Ru, Ni, Cu > Fe.

One of the most important problems is the question of crystal solvent molecules. In some cases, complexes without crystal solvent molecules are formed in other cases the crystal solvent molecules occur in low or high amounts. The hydrogen bonding network or van der Waals interactions are expected to bind these solvent molecules inside the crystal structure.

It seems that the conditions of complex preparation play one of the most important roles in the final product. The following factors are the most important: (i) the solvent or mixtures of solvent used; (ii) the molar ratio M:L used; (iii) the counter anion used; (iv) the method of preparation. It seems that the solvent or mixtures of solvents used plays a more important role than even the stoichiometric ratio M:L. The majority of complexes have composition corresponding to the molar ratio of the reactants. Moreover, the molecules of solvents or counter anions used are involved in hydrogen bonding whenever possible. By minor differences in the mixtures of solvent used, different compounds can be prepared from the same stating materials used in the same molar ratio. The compounds formed may have completely different magnetic properties and molecular structure, as well as other properties.

In some cases, the complexes with the deprotonated form of the ligand *bzimpy* were obtained without addition of any base. Here the following points can play a role: (i) acid-basic properties of the solvents, counter anions or ligands; (ii) coordination properties of the solvent, counter anions or ligands; (iii) nature of the central atom in terms of Lewis acid-basic properties or metal ion radii; (iv) other conditions such as temperature, concentration, etc. The deprotonation itself, and even its rate, depends on a delicate balance between all these conditions. If the other base is implemented in the system, then deprotonation will be the most likely resulting process.

One can suppose that in the case of bis-ligand complexes (FeL$_2$(X$_2$ the magnetic properties depend upon the counter anion X$^-$ or solvent molecules present and in the case of mono-ligand complexes (FeLY$_2$] (L = *bzimpy* or *bztpy*) the magnetic behaviour is strongly affected by the ligand field strength of the co-ligands Y.

The ligand field strength of the tris-imine system must be very close to the critical value so that a transition occurs between the $^1A_{1g}$ and $^5T_{2g}$ states of the $\{FeN_6\}$ system. The complex (Fe(terpy)$_2$(Br$_2$·H$_2$O is diamagnetic at room temperature. According the above, one can suppose a higher ligand field strength of the terpyridine relative to the *bztpy* ligand. Moreover, one can expect a dependence of the magnetic properties of the cation (Fe(bztpy)$_2$($^{2+}$ on the quality of the counter-anion.

The complex (Fe(bztpy)$_2$((ClO$_4$)$_2$·S (S = solvent) exhibits a complete LS to HS conversion, unlike (Fe(bzimpy)$_2$((ClO$_4$)$_2$·S. This could be caused by a lowering of the ligand field strength when the benzimidazole group is replaced by benzthiazole [29]. A more important result is that for both Fe(III) ([Fe(bztpy)$_2$](ClO$_4$)$_3$·2CHCl$_3$·3H$_2$O) and Fe(II) ((Fe(bztpy)$_2$((ClO$_4$)$_2$·3H$_2$O) complexes of the same ligand *bztpy* features of spin crossover were observed. Such an observation is unique.

UV/vis spectra of the mono-ligand [Cu(II)L]$^{2+}$ complexes showed that *bzimpy* is a significantly weaker donor than *bztpy* [160]. This corresponds to studies of bis-ligand [Fe(II)L$_2$]$^{2+}$ complexes. Complexes with *bzimpy* are LS while complexes with *bztpy* are HS [80] (see, however, Section 3.1.5.1).

In the solid state, bands for the LS state and the HS state can be observed separately. In solution they overlap one another. This indicates that the difference in energies of the ligand fields ($\Delta_0 = \Delta_{LS} - \Delta_{HS}$) between the two spin states is lowered in solution, supporting the theory proposing that lattice deformation forces play an important role in the solid state.

A correlation was observed between the spin state of iron salts with bis-(tri-imino)-ligands and absorbance bands in the solid state. A weak broad band (likely d–d transition) occurs at 10,500 cm^{-1} for HS complexes but is absent for LS complexes. In the UV/vis spectra of complexes the details are solvent-dependent [29]. The differences between the Δ_0 values in the solid state explain the difficulty of predicting the spin crossover in solution on the basis of measurements in the solid state. Spin crossover behaviour of the complex (Fe(X-bzimpy)$_2$($^{2+}$ (X = H) in solution is strongly reduced by replacing the hydrogen atom by electron withdrawing substituents and this leads to an almost HS state at room temperature [33]. The order of energies of the MLCT band is: *bzimpy*$_{-H}$ < *bzimpy* < *bztpy* in iron(II) complexes [80].

The series of copper complexes with the ligand *bzimpy* was studied by solution chemistry. Comparison of the energies of d–d transitions of the complexes (CuL($^{x+}$, (CuLCl($^{x+}$ and (CuLOH($^{x+}$ (L = *bzimpy, mbzimpy, terpy, bztpy, bzoxpy*) revealed that the ligands *bzimpy* and *mbzimpy* are comparable in ligand field strength to *terpy* whilst ligands *bztpy* and *bzoxpy* are significantly weaker ligands in terms of ligand field strength [160]. This statement was confirmed by Mössbauer spectra. The complexes involving (FeL$_2$($^{2+}$ are in LS state when L = *bzimpy* and *mbzimpy* or in HS state when L = *bztpy*, *bzoxpy* at room temperature. EPR spectra in solution for (CuL($^{x+}$ complexes indicate a tetragonal structure. A detailed analysis of solutions of complexes revealed that ligands *bztpy* and *bzoxpy* dissociate (decomplexate) very easily in the presence of other ligands or in solvents with strong donor properties [160].

The above Review contains only selected data from the original work. However, other important data can be found there starting from all possible spectroscopic analysis through to electrochemical investigations arising from potentials for different applications.

A rational modification of the ligand system and the packing in the solid state are promising tools for tuning properties of interest such as spin crossover above room temperature. However, the most important complication is the presence of crystal water (or other solvents) that is liberated upon heating above room temperature.

Coming through the reported data one can observe a development of selected properties and can easily identify the blind spots. Even though a variety of complexes was prepared, there is still a huge number of complexes that have not been investigated as analogues of known compounds. In addition, many different systems have no representative compounds, e.g. d^2 or d^4 systems for ligand *bzimpy* and d^0–d^4 for the ligand *bztpy*. On the other hand, many metals still have not been studied e.g. Hf, Ta, Nb or Ti and others.

Complexes containing the N-substituted ligand *bzimpy* were reported over a wide range of central metal atoms and their chemistry, structural properties and numerous different applications were described in detail, e.g. [18–22,45,46,66,155,166,188–207].

Acknowledgements

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Appendix A.

See Tables A1 and A2.

Appendix B.

See Tables A3 and A4.

Appendix C.

A bibliography of non-English papers or non-accessible ones.

Synthesis, characterization and interaction with DNA of copper(II) complex with 2,6-bis(benzimidazole-2′)pyridine and glycine [208].

Abstract: The Cu(II) complex [CuL(Gly)]NO$_3$·H$_2$O was synthesized and characterized by UV, IR spectroscopy and fluorescence spectra, where L is 2,6-bis(benzimidazole-2′)pyridine, gly is glycine. The binding of the complex with calf thymus DNA was investigated by UV, fluorescence spectra, and viscosity measurements. The complex binds to DNA base pairs by partial intercalation.

Synthesis of europium(III) complex and its interaction with DNA [209].

Abstract: A europium(III) complex with H$_2$bzimpy having planar tridentate ligand was synthesized and characterized by UV, IR spec-

Table A1
Different notation and abbreviations of the ligand 2,2′-pyridine-2,6-diylbis(1H-benzimidazole) and its protonated or deprotonated forms in the literature[a,b].

Non IUAC names	Ref.	Abbreviation	Ref.
2,6-Bis-(2-benzimidazyl)pyridine	[40,55,87,100,178,182]	bzp	[61]
2,6-Di(2-benzimidazolyl)pyridine	[55]	bimpyH_2	[106,107]
2,6-Bis(benzimidazol)pyridine	[23,105,109,111,112,175]	bBziH_2py	[23,39,40,49,178]
2,6-Bis(benzimidazole)pyridine	[138]	bbpH_2	[105,111]
2,6-Bis(2-benzimidazol-2-yl)pyridine	[96]	H_2bbipy	[47]
2,6-Bis(benzimidazolyl)pyridine	[49,63,98,168,171,173]	pimH_2	[86]
2,6-Bis(2-benzimidazolyl)pyridine	[47,54,65,81,84,101,154,161, 163,165,179]	bbimpy	[84,163]
2,6-Bis(benzimidazol-2-yl)pyridine 2,6-Bis(benzimidazol-2′-yl)pyridine	[24,25,29–32,34–36,41,43,50,51, 57–59,82,83,85,90–95,97,102–104, 106–108,110,130,132–135, 139–148,155–157,160,162,169,170, 172,174,176,177,180,181]	bzimpy	[25,29–32,35,36,44,50,83,85, 91–96,99,103,104,108,109, 130–135,137–148,150, 159–161,164,169,170]
2,6-Bis(1H-benzimidazol-2-yl)pyridine	[62,64,153,167]	bbip	[24,62,153,177]
2,6-Bis(benzimidazo-2-yl) pyridine	[44,159,164]	$(BzImH)_2$py	[173,179]
2,6-Bis(benzimidazole-2-yl)pyridine	[26,27,61,151,166]	BBP	[41,90,98,110,154,168,171, 172,174–176,181,182]
2,6-Bis(benzimidazoly-2-yl)pyridine	[99]	bzmpy	[158]
2,6-Bis-(2-bezimidazyl)pyridine	[39]	bbipH_2 H_2bbip	[42,100,101]
2,6-Bis(2-benzimidazol)pyridine	[150]	H_2bzimpy	[57,82]
Bis(benzimidazol-2-yl)pyridine	[131]	Bbzlpy	[26,27,87]
2-[6-(1H-Benzimidazol-2-yl)-2-pyridyl]-1H-benzimidazol-3-ium[c]	[74]	bbpy	[48]
2,6-Bis(benzoimidazolyl)pyridine	[56]	bbzly	[151]
2,6-Bis(benzimidazyl)pyridine	[27]		
2,6-Bisbenzimidazylpyridine	[48]		

[a] A frequent mistake is also the use of “benzimidazole” instead of “benzimidazol” inside the name.
[b] In the remaining literature the notation 2,6-bis-(benzimidazol-2-yl)-pyridine is used.
[c] IUPAC nomenclature.

Table A2
Different abbreviations of the ligand 2,2′-pyridine-2,6-diylbis(1,3-benzothiazole) in the literature.

Non IUAC names	Ref.	Abbreviation	Ref.
2,6-Bis-(benzthiazol-2-yl)-pyridine	[28]	bztpy	[28,29]
2,6-Bis(benzothiazol-2-yl)pyridine	[29,68,160,186,187]	bzthpy	[80,160,186]
2,6-(Dibenzothiazol-2-yl)pyridine	[72,183]	dbtp	[183]
2,2′-(Pyridine-2,6-diyl)bisbenzothiazole	[185]	pbbt	[185]
		bbzthpy	[187]

troscopy, and fluorescence spectra, wherein H_2bzimpy was 2,6-bis (benzimidazole-2′-yl)pyridine. The binding of this complex with calf thymus DNA had been investigated by absorption, luminescence titration, and viscosity measurements. The results suggested that europium(III) complex partly intercalated into DNA base pairs via the ligand H_2bzimpy.

Chromogenic reaction of 2,6-bis(benzimidazol-2′-yl)pyridine with cobalt(II) [210].

Abstract: In the medium of HOAc–NaOAc with pH 3.5–4.5, 2,6-bis (benzimidazole-2′-yl)pyridine reacts with Co(II) and forms a 3: 1 stable green complex with a max. absorption wavelength at 360.6 nm and the apparent molar absorptivity of $4.467 \times 10^4\,\mathrm{L\,mol^{-1}\,cm^{-1}}$. Beer’s law is obeyed at 0–20 μg/25 mL for Co(II). The method was used for the direct determination of Co in vitamin B_{12} and molecular sieve containing Co with satisfactory results.

Metal/2,6-bis(benzimidzolyl)pyridine binding: towards metallo-supramolecular polymers [211].

Abstract: We have prepared a monomer unit which has two tridentate ligands, derived from 2,6-bis-(benzimidazolyl)pyridine, attached to either end. This bis-ligand monomer was combined with perchlorate salts of Zn(II), Cd(II), Fe(II), and Co(II) in a ratio of 2:1 ligand to metal ion with the intent to form macrocycles and/or linear polymeric species. UV–vis and ^{1}H-NMR titration experiments were performed on the metal/ligand complexes to determine the overall association constants and the kinetics of dissociation. These binding constants were on the order of 108 $\mathrm{M^{-1}}$ and were verified through the use of a model mono-ligand compound The Cd(II) complexes exhibited the fastest kinetics of dissociation of the systems investigated so far.

A study on the ATRP polymerization initiated by a new kind of Cu(I) complex [212].

Abstract: 2,6-Bis(2-benzimidazolyl) pyridine as a tridentate ligand for the Cu(I) complex formation used in the initiation system of ATRP has been studied. The complex obtained possesses favourable catalytic activity for the initiation of polymerization in which the ATRP characteristic is evident. Compared with the rate of polymerization initiated from Cu(I) complex composed of different ligands with various amines, obtained results are consistent with the known order as follows: alkyl amine ≈ pyridile > imine > aryl amine.

Synthesis of 2,6-bis(2-benzimidazolyl)pyridine under microwave-irradiation using PPA as a catalyst and solvent [213].

Abstract: A novel microwave-enhanced synthesis of 2,6-bis(benzimidazolyl-2′)pyridine (I) by the sufficient mixing of o-phenylenediamine with pyridine-2,6-dicarboxylic acid, using polyphosphoric acid (PPA) as a catalyst and solvent, has been developed for the first time. The yields are the same as conventional synthesis, and the reaction rate in this condition is 80 times as that in conventional synthesis condition, so the reaction time is greatly reduced. Moreover the optimum synthesized condition under microwave irradiation has been explored.

Synthesis and characterization of tridentate polypyridyl cobalt(III) and ruthenium(II) complexes and its interaction with DNA [214].

Table A3
Complexes with 2,6-bis-(benzimidazol-2-yl)-pyridine (*bzimpy*) known up to date and all transferred to our notation.

	Mono-ligand complexes	Bis-ligand and tris-ligand complexes
d^0	$[Zr(bzimpy_{-2H})Cl_2]$ [47] $[VO_2(bzimpy_{-H})]\cdot 1.25H_2O$ [82] $Na_2(bzimpy_{-2H})$ [34] $Li_2(bzimpy_{-2H})$ [34]	$[\{MoO(O_2)_2\}_3(bzimpy)_2]^a$ [83] $[\{WO(O_2)_2\}_3(bzimpy)_2]^a$ [83]
d^1	$[VO(bzimpy)(H_2O)_2](CF_3SO_3)_2\cdot 2H_2O$ [82]	
d^3	$[Cr(bzimpy)Cl_3]$ [84] $[(\mu\text{-}O)\{ReOCl_2(bzimpy_{-H})\}_2]\cdot 2H_2O\cdot 2DMF$ [86]	$[Cr(bzimpy_{-H})_2]Cl$ [85]
d^5	$[Mn(NO)_2(CN)_2(bzimpy)]\cdot H_2O$ [87] $[Mn(bzimpy)X_2]$ (X = Cl [90], Ac [90]) $[Mn(bzimpy)Cl_2]\cdot S$ (S = DMFA [90], 0.5MeOH [91–94]) $[Fe(bzimpy)Cl_3]$ [29,98] $[Ru(bzimpy)Cl_3]$ [100,102] $[Ru(bzimpy_{-H})(bpy)Cl][PF_6]$ (X = Cl, NO_3) [100] $[Ru(bzimpy_{-H})(L)_2][(PF_6)_2]$ (L = 2,2′-bipyridine, 1,10-phenantroline) [100] $Ru(bzimpy_{-H})(phen)Cl][PF_6]$ [100] $[Ru(bzimpy_{-H})L^{a1}DMSO](PF_6)_2$ (L^{a1} = aryl-azo pentane-2,4-dione ligands) [101] $[Ru(bzimpy_{-H})(L)(pyz)(L)(bzimpy_{-H})Ru][(PF_6)_3]$ (L = 2,2′-bipyridine, 1,10-phenantroline; pyz = pyrazine) [100]	$[Mn(bzimpy)_2(SO_4)]\cdot 4H_2O$ [90] $[Mn(bzimpy)_2]X_2\cdot 3H_2O$ (X = NO_3, ClO_4) [90] $[Mn(bzimpy)_2](ClO_4)_2$ [36,91,144] $[Mn(bzimpy_{-H})_2]$ [95,96] $[Mn(bzimpy_{-H})_2]\cdot$etylacetate$\cdot H_2O$ [97] $[NHEt_3][Fe(bzimpy_{-2H})_2]\cdot 4H_2O$ [29] $Fe(bzimpy)_2(BF_4)_3\cdot 0.5EtOH$ [60] $[Fe(bzimpy)_2](ClO_4)_3$ [99] $Fe(bzimpy)_3(ClO_4)_3\cdot S$ (S = $2H_2O$, $2H_2O\cdot 2EtOH$) [60] $[Ru_2(bzimpy_{-H})_2L^{a2}Cl_2](PF_6)_2$ (L^{a2} = aryl-azo pentane-2,4-dione ligands) [101]
d^6	$RhX_3(bzimpy)$ (X = Cl, Br, I) [23] $[RhX_2(CO)(bzimpy)]X$ (X = Cl, Br) [23] $IrX_3(bzimpy)$ (X = Cl, Br) [23] $[RuL(bzimpy)](PF_6)_2$ (L = see [106]) $[Ru(PPh_3)_2(bzimpy)Cl]Cl\cdot CHCl_3\cdot H_2O$ [105] $[Ru(PPh_3)_2(bzimpy)Cl]Cl$ [111] *trans*-$[Ru(PPh_3)_2(bzimpy)(CH_3CN)](ClO_4)_2\cdot 2H_2O$ [111] $[Ru(NO_2)(bzimpy)(PPh_3)_2](ClO_4)\cdot EtOH$ [112] $[Ru(bzimpy)(bpy)Cl]Cl$ [109] $[Ru(bpy)(bzimpy)Cl](ClO_4)$ [111] $[Ru(bpy)(bzimpy)Cl](ClO_4)\cdot 0.5Et\text{-}O\text{-}Et$ [111] $[Ru(bzimpy)(phen)Cl]Cl$ [109] $[Ru(bzimpy)(bpy)(OH_2)](ClO_4)_2$ [109] $[Ru(bzimpy)(phen)(OH_2)](ClO_4)_2$ [109] $[Ru(bzimpy_{-2H})L(CH_3CN)]$, $[Ru(bzimpy_{-2H})L(CH_3CH_2NH_2)]$ (L = o-phenylenediamine) [110] $[Ru(bzimpy_{-H})(bpy)Cl]$ [100] $[Ru(terpy)(bzimpy)](ClO_4)_2$ [111] $[Ru(trpy)(bzimpy)](ClO_4)_2\cdot 2H_2O$ [108] $[Ru(trpy)(bzimpy_{-2H})]\cdot 2H_2O$ [108] $[Ru(trpy)(bzimpy)](ClO_4)_2\cdot MeOH$ [108] $[ReBr(CO)_3(bzimpy)]$ [24]	$[Fe(bzimpy)_2](ClO_4)_2\cdot nH_2O$ ($n = 0$ [29,32,33,35,36,50,59,130–132,142–144,146–148] $n = 0.25$ [31,61,133–136,140], $n = 1$ [80]) $[Fe(bzimpy)_2][FeCl_4]$ [29] $[Fe(bzimpy)_2](BPh_4)_2\cdot nH_2O$ ($n = 0, 2, 4$) [30,136] $[Fe(bzimpy_{-H})_2]\cdot nH_2O$ ($n = 0.5$ [80], $n = 1$ [29,139–141], $n = 2$ [61,138]) $[Fe(bzimpy)_2](CF_3SO_3)_2\cdot S$ (S = 2EtOH [80], H_2O [80]) $[Fe(bzimpy)_2](SO_4)_2\cdot 2H_2O$ [30] $[Fe(bzimpy)_2]Cl_2\cdot S$ (S = MeOH [29], $2H_2O$ [80]) $[Ru(bzimpy)_2](PF_6)_2$ [58] $[Ru(bzimpy)_2](ClO_4)_2\cdot 2H_2O$ [58] $[Co(bzimpy_{-H})_2]OH$ [34] $[Ru(bzimpy)_2]Cl_2$ [102,104] $[Rh(bzimpy)_2(OClO_3)](ClO_4)_2$ [23] $[Ru(bzimpy_{-H})_2]$ [100]
d^7	$[Co(bzimpy)X_2]$ (X = Cl [41,92–94], Br [40], I [40]) $[Co(bzimpy)Cl(MeOH)_2]Cl$ [41] $[Co(bzimpy)(MeOH)Cl]Cl\cdot MeOH$ [149] $[Co(bzimpy)(H_2O)_2Cl]Cl\cdot 2H_2O$ [150]	$[Co(bzimpy)_2](ClO_4)_2$ [36,41,57,144] $[Co(bzimpy)_2(ClO_4)](ClO_4)$ [40] $[Co(bzimpy)_2](SO_4)_2\cdot H_2O$ [41] $[Co(bzimpy)_2](NO_3)_2\cdot H_2O$ [41] $[Co(bzimpy)_2]X_2\cdot 2H_2O$ (X = Cl, Br, I) [40] $[CoCl(bzimpy)_2]Cl\cdot 2H_2O$ [49] $[Co(bzimpy)_2(pa)_2]$ (pa = picric anion) [151] $[Co(bzimpy_{-H})_2]\cdot 2H_2O$ [41] $[Co(bzimpy)_2]Cl(OH)\cdot 3H_2O$ [150] $[Co(bzimpy_{-H})_2]$ [103]
d^8	$[Ni(N_3)(bzimpy)(MeOH)MeO]$ [154] $[Ni(bzimpy)X_2]$ (X = Cl, Br) [40] $[Ni(ths)(bzimpy)(dmf)]\cdot H_2O$ [153] $[Ni(NCS)_2(bzimpy)(H_2O)_2]$ [26] $[Pd(cotl)(bzimpy)](ClO_4)$ [156] $[\{PdX(cotl)\}_2(bzimpy)]$ (cotl = cyclooctenyl, X = Cl or Br) [156] $[Pd(bzimpy)Cl_2]$ [155] $[Pd(bzimpy)Br_2]$ [155] $[Pd_2(bzimpy)_3(ClO_4)](ClO_4)\cdot 2H_2O$ [155] $[Pt(bzimpy)Cl](PF_6)$ [44] $RhX(bzimpy)\cdot 2H_2O$ (X = Cl, Br) [23] $RhX(CO)_2(bzimpy)\cdot 1.5H_2O$ (X = Cl, [23,49], X = Br [23]) $Rh(bzimpy)(CO)_2(OClO_3)$ [23] $IrX(CO)_2(bzimpy)\cdot nH_2O$ (X = Cl, $n = 1$; X = Br, $n = 1.5$) [23]	$[Ni(bzimpy)_2]X_2\cdot H_2O$ (X = Cl, Br, I) [40] $[Ni(bzimpy)_2](ClO_4)_2\cdot nH_2O$ ($n = 0$ [33,36,40,144], $n = 1$ [55]) $[Ni(bzimpy)_2](BPh_4)_2\cdot H_2O$ [55] $[Ni(pa)_2(bzimpy)_2]$ (paH = picric acid) [27]
d^9	$[Cu(bzimpy)(H_2O)_2(ONO_2)](NO_3)\cdot H_2O$ [163] $[Cu(bzimpy)NCMe(ClO_4)](ClO_4)$ [157,158] $[Cu(bzimpy)(ClO_4)_2]\cdot nH_2O$ ($n = 2$ [157], $n = 3$ [160]) $[Cu(bzimpy)(NO_3)_2]\cdot 2H_2O$ [157] $[Cu(bzimpy)(ClO_4)Cl]\cdot H_2O$ [166]	$[Cu(bzimpy)_2](ClO_4)_2$ [157] $[Cu(bzimpy)_2]Cl_2\cdot EtOH\cdot H_2O$ [60]

Table A3 (*Continued*)

	Mono-ligand complexes	Bis-ligand and tris-ligand complexes
	$[Cu (bzimpy)Cl_2]$ [165] $[Cu(bzimpy)Cl_2]\cdot S$ (S = $2H_2O$ [157], DMFA [160,161]) $Cu(bzimpy)(OAc)_2$ [56] $[Cu(bzimpy)Br_2]\cdot 0.5H_2O$ [157] $Cu(bzimpy_{-2H})\cdot 0.75EtOH$ [60] $[Cu(bzimpy)Cl]Cl$ [159] $[Cu(bzimpy)Cl(H_2O)O_2]Cl$ [164] $[(bzimpy)\text{-}Cu\text{-}\mu\text{-}Cl_2\text{-}Cu\text{-}X]$ (X = Cl, I, SCN) [165]	
d^{10}	$[Zn(bzimpy)Cl_2]\cdot 2H_2O$ [157] $[Zn(bzimpy)Cl_2]$ [59] $[Zn(bzimpy)Cl_2]\cdot DMF$ [167,168] $[Zn(bzimpy)Cl_2]\cdot MeOH$ [168] $[Zn(bzimpy)(p\text{-}CPOA)]_n$[a] [171] $[Zn(bzimpy)(p\text{-}pdoa)]_n$[a] [172] $[Zn(bzimpy)TDT]$ (TDT = 3,4-toluenedithiolate) [173] $[Zn(bzimpy)Br_2]\cdot H_2O$ [157] $[Zn(bzimpy)NO_3](NO_3)$ [169] $[Cd(bzimpy)Cl_2]\cdot H_2O$ [174] $[Cd(bzimpy)Cl_2]\cdot$[59] $[Cd(bzimpy)Cl_2]\cdot DMF$ [175] $[Cd(bzimpy)(ClO_4)](ClO_4)$ [39] $[Cd(bzimpy)(NO_3)_2]\cdot 0.5H_2O$ [174] $[Cd(bzimpy_{-H})(OAc)]$ [174] $[Cd(bzimpy)(p\text{-}PDOA)]_n$ [176] $Cd_2(bzimpy)_2(Ac)_3\cdot 0.5S_2O_8\cdot 2H_2O$[a] [177] $[Hg(bzimpy)Cl_2]$ [59] $[Hg(bzimpy)Cl_2]\cdot 2DMF$ [63] $[Hg(bzimpy)(ClO_4)](ClO_4)$ [39] $[Ag(bzimpy)](ClO_4)$ [178] $[In(bzimpy_{-H})Cl_2(H_2O)]\cdot DMF$ [175] $[Pb(bzimpy)(H_2O)_2(NO_3)_2]\cdot bzimpy\cdot H_2O$ [179]	$[Zn(bzimpy)_2](ClO_4)_2\cdot nH_2O$ ($n = 0$ [36,144], $n = 2$ [170], $n = 3$ [80]) $[Zn(bzimpy)_2(ClO_4)](ClO_4)$ [39] $[Zn(bzimpy_{-H})_2]$ [42,43] $[Cd(bzimpy_{-H})(bzimpy)]X$ (X = ClO_4, BF_4) [174] $[Cd(bzimpy_{-H})_2]$ [43,174]
f^n	$[Lu(bzimpy_{-H})(NO_3)_2(OH_2)]\cdot 2H_2O$ [181] $[Lu(bzimpy_{-H})(NO_3)_2(MeOH)_2]\cdot(bzimpy)\cdot 2MeOH$ [25]	$[Ln(bzimpy)_2(NO_3)_2](NO_3)\cdot nMeOH$ (Ln = Eu, $n = 0, 2$, [180]; Ln = Ce, $n = 0, 3$ [180]; Ln = Sm, $n = 0$ [180], Ln = Tb, $n = 0, 2$ [180]) $[Ln(bzimpy)_2(NO_3)_2](NO_3)\cdot H_2O$ (Ln = La, Ce, Nd, Pr, Eu, Gd, Tb) [181] $[Sm(bzimpy)_2(NO_3)_2](NO_3)\cdot 2H_2O$ [181] $[Dy(bzimpy)(bzimpy_{-H})(NO_3)(OH_2)](NO_3)\cdot 4H_2O$ [181] $[Er(bzimpy)(bzimpy_{-H})(NO_3)(OH_2)](NO_3)\cdot 3H_2O$ [181] $[U(bzimpy)_3Cl_4]\cdot xTHF$ [182]

[a] Polynuclear complex.

Table A4

Complexes with 2,6-bis-(benzthiazol-2-yl)-pyridine (*bztpy*) known up to date.

	Mono-ligand complexes	Bis-ligand complexes
d^5	$(Mn(bztpy)Cl_2(\cdot 0.5H_2O$ [72] $Mn(bztpy)(ClO_4)_2$ [28] $[Fe(bztpy)Cl_3]\cdot CHCl_3$ [28] $[Fe(bztpy)Cl_3]\cdot MeNO_2$ [28] $Fe(bztpy)(NO_3)_3\cdot 1.5CHCl_3\cdot MeOH$ [28] $(Ru(bztpy)Cl_3(\cdot C_2H_5OH$ [183] $[Ru(bztpy)Cl_3]$ [102]	$(Fe(bztpy)_2Cl_3(\cdot H_2O$ [183] $[Fe(bztpy)_2](ClO_4)_3\cdot S$ (S = $2CHCl_3\cdot 3H_2O$, $CHCl_3\cdot 3H_2O$, $2CHCl_3\cdot H_2O$) [28] $[Fe(bztpy)_2](NO_3)_3\cdot 2.5CHCl_3$ [28] $[Fe(bztpy)_2](BF_4)_3$ [28] $(Fe(bztpy)_2(Br(FeBr_4($ [72,185]
d^6	$(Fe(bztpy)Cl_2(\cdot 0.5H_2O$ [72] $(Fe(bztpy)X_2(($X = Br [72], I [72,185], NO_3 [28], ClO_4 [60]) $(Fe(bztpy)(NCS)_2(\cdot 0.5H_2O$ [72,185] $Fe(bztpy)(phen)(ClO_4)_2\cdot CHCl_3$ [28] $(Rh(bztpy)Cl_3(\cdot 2H_2O$ [183]	$(Fe(bztpy)_2((ClO_4)_2\cdot S$ (S = $4H_2O$ [80], $3H_2O$ [72,80,185], $0.75CHCl_3$ [80], $CHCl_3$ [29]) $[Fe(bztpy)_2](BPh_4)_2\cdot 2CHCl_3$ [28] $[Ru(bztpy)_2]Cl_2$ [102] $[Ru(bztpy)_2](PF_6)_2\cdot DMF$ [186]
d^7	$(Co(bztpy)Cl_2(\cdot 0.5H_2O$ [72] $(Co(bztpy)Br_2($ [72] $(Co(bztpy)(NCS)_2($ [72] $(Co(bztpy)(NO_3)_2($ [72] $(Co(bztpy)I_2($ [183] $Co(bztpy)(PF_6)_2\cdot 4H_2O$ [60]	$(Co(bztpy)_2((ClO_4)_2\cdot 5H_2O$ [72] $[Co(bztpy)_2((BF_4)_2\cdot 4H_2O$ [72] $[Co(bztpy)_2]X_2\cdot CHCl_3$ (X = CF_3SO_3 [28], BF_4 [60])
d^8	$[Ni(bztpy)Cl_2]$ [72] $[Ni(bztpy)(NO_3)_2]$ [72] $(Pd_2(bztpy)Cl_4($ [183]	$(Ni(bztpy)_2((ClO_4)_2\cdot S$ (S = $2H_2O$ [183], $CHCl_3$ [28])
d^9	$(Cu(bztpy)Cl_2(\ H_2O$ [183] $(Cu(bztpy)Cl((ClO_4)$ [160] $(Cu(bztpy)((ClO_4)_2$ [160] $(Cu(bztpy)Br_2($ [183]	–
d^{10}	$(Zn(bztpy)Cl_2($ [183] $Zn(bztpy)X_2\cdot nH_2O$ ($n = 1$, X = Cl; $n = 0$, X = Br, I) [187] $(Hg(bztpy)X_2($ (X = Cl, Br) [183] $Ag(bztpy)ClO_4$ [183]	$(Zn(bztpy)_2((ClO_4)_2\cdot 3H_2O$ [80] $(Zn(bztpy)_2(H_2O)((ClO_4)_2\cdot H_2O$ [187]

Abstract: Two novel tridentate polypyridyl mixed-ligand complexes of cobalt(II) and ruthenium(II), $[Co(TolylTPy)(H_2Bzimpy)]Cl_2$ [TolylTPy = 4′-p-tolyl-2,2′:6′,2″-terpyridine, H_2Bzimpy = 2,6-bis(benzimidazol-2-yl)pyridine] (A) and Ru(TolylTPy) (Bzimpy) (B) were synthesized and characterized by elemental analysis, IR and ^{1}H NMR. The crystal structure of complex B was determined The interactions between the complexes and calf thymus DNA have been investigated by absorption and fluorescence spectroscopies. The photoactivated cleavage of pBR322 DNA by the complexes was studied. The spectrophotometric studies suggested that both complexes A and B bind to DNA by electrostatic interactions. The agarose gel electrophoresis showed that complex A converted supercoiled pBR322 DNA to nickel and linear DNA when it was irradiated at 310 nm for 15 min.

Synthesis, characterization and DNA-binding studies of new tridentate polypyridyl cobalt(II) and ruthenium(II) complexes [215].

Abstract: Two novel tridentate polypyridyl mixed-ligand cobalt(III) $[Co(PhTPY) (H_2Bzimpy)]^{3+}$(A) and ruthenium(II) [Ru(PhTPY) (Bzimpy)](B) complexes were synthesized and characterized via elemental analysis and ^{1}H NMR. The crystal structure of complex B was determined. The interactions between the complexes and calf thymus DNA were investigated with absorption and fluorescence spectroscopies. Photoactivated cleavage of pBR322DNA by the synthesized complexes were studied. The spectrophotometric studies show that the modes of these two complexes interacting with DNA were electrostatic interaction. The agarose gel electrophoresis results show that complex A and complex B converted supercoiled pBR322DNA to nicked and linear DNA when irradiated by the light with a wavelengths 310 nm for 15 min, 450 nm for 4 min, resp.

There's something dangling on my ruthenium [216].

Abstract: The tetradentate thioethers, 1,9-Bis(2′-pyridyl)-3,7-dithianonane (Pdtn), 1,10-Bis(2′-pyridyl)-3,8-dithiadecane (Pdtd) and 1,2-bis((2-(2′-pyridyl)ethylthio)methyl)benzene (Pemb) were used to form dinuclear ruthenium(II) complexes of the type $[Ru_2(L1)_2(m\text{-}Cl)_2]^{2+}$ via reaction with $RuCl_3{\cdot}xH_2O$. Upon reaction of the dinuclear complexes with the triimine ligands 2,6-bis(benzimidazolyl)pyridine (Bzimpy) and 2,6-bis(N′-methylbenzimidazolyl)pyridine (Me_2Bzimpy), facile symmetry bridge cleavage occurs, producing mononuclear complexes of the form $[Ru(L1)(L2)]^{2+}$, where L1 is one of the three tetradentate thioether ligands and L2 is one the triimine tridentates. In the mononuclear complexes, one of the pyridine arms of the tetradentate thioether is forced to be uncoordinated, due to the firmly hexacoordinate nature of Ru(II). The pyridine is thus able to bind a Lewis-acid Cu(II) moiety. Both the mononuclear and the dinuclear Ru(II) complexes are luminescent and the redox chemistry of the dinuclear complexes shows two oxidative steps.

Synthesis, crystal structure and fluorescence spectrum of an ionic compound $[2,6\text{-bis(benzimidazol-2-yl)pyridine}H_2]^{2+}{\cdot}[SbCl_5]^{2-}$ [217].

Abstract: A ionic compound $[2,6\text{-bis(Benzimidazol-2-yl)pyridine}H_2]^{2+}{\cdot}[SbCl_5]^{2-}$ was synthesized by the hydrothermal reaction of o-phenylenediamine, pyridine-2,6-dicarboxylic acid with $SbCl_3$ in 1:1 HCl solution. The compound was characterized by chemical analysis, elemental analysis, TG-DTA, fluorescence spectrum and IR spectra. The single crystal structure was determined by X-ray single crystal diffraction. It crystallizes in triclinic system, space group P-1 with: $a = 0.987\ 2(10)$ nm, $b = 1.133\ 32(11)$ nm, $c = 1.182\ 4(2)$ nm, $\alpha = 108.269(10)^{\circ}$, $\beta = 100.807(10)^{\circ}$, $\gamma = 107.523(10)^{\circ}$, $Z = 2$, $V = 1.138\ 4(3)$ nm^3, $Dc = 1.786$ g cm^{-3}, $\mu = 1.816$ mm^{-1}, $F(000) = 600$, R1 = 0.0220, wR2 = 0.057 1. The single crystal structure indicates that the antimony ion to five Cl^- forms a coordination structure of distorted square pyramid. Two $[SbCl_5]^{2-}$ form four-member ring by secondary bonding Sb(1)···Cl(1)ii, and the four-member ring with 2,6-bis(benzimidazol-2-yl)pyridine cation forms the three-dimensional reticulation ionic crystal by ionic bonds and hydrogen bonds. It has been proved that the title compound has fluorescence behaviour.

Synthesis, crystal structure and luminescent properties of rare earth picrate complexes with 2,6-bis(benzimidazol-2-yl)pyridine [218].

Abstract: Solid complexes of rare earth picrates (pic) with the ligand 2,6-bis(benzimidazol-2-yl)pyridine (L) have been synthesized and characterized by elemental analysis, IR and electronic spectra. The crystal and molecular structures of the complex $[CeL_2(pic)_2](pic){\cdot}(CH_3OH)_3$ have been determined by single crystal X-ray diffraction. The crystal structure indicates that the complex crystallizes in the triclinic space group *P*-1 with parameters: $a = 1.3795(3)$ nm, $b = 2.1292(5)$ nm, $c = 2.5651(6)$ nm, $\alpha = 105.847(3)^{\circ}$, $\beta = 100.150(3)^{\circ}$, $\gamma = 107.893(3)^{\circ}$, $Z = 2$, $R = 0.0519$, wR = 0.1255. The crystal consists of two similar but independent molecules in the asymmetric unit and the Ce(III) ion coordinated toward ten donor atoms, six of which belong to the nitrogen atoms of two tridentate ligands and four oxygen atoms from two bidentate picrates. The coordination polyhedron around Ce^{3+} is a distorted square antiprism, and the two independent molecules are connected by π–π stacking interactions to form a noncentrosymmetric dimer. The crystal structure is built of a packing of these dimers via intermolecular hydrogen bonding to yield an infinite three-dimensional supramolecular network. At room temperature, under UV light excitation the Eu(III) complex exhibited characteristic emission of the central metal ions both in solid state and in solutions.

Proton NMR studies on 2,6-bis(benzoimidazol-2′-yl)pyridine and its ruthenium(II) complex [219].

Abstract: ^{1}H NMR of 2,6-bis(benzoimidazal-2-yl)pyridine and its Ru(II) complex were assigned by HOMO decoupling method.

Appendix D. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ccr.2010.09.010.

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