Supramolecular Detection of Metal Ion Binding: Ligand Conformational Control of Cholesteric Induction in Nematic Liquid Crystalline Phases

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Abstract: Tripodal tetradentate ligands may act as chemosensor molecules. Their ability to torque a nematic into a cholesteric phase increases upon complexation with copper ion. Moreover, changes in overall shape of the complexes induced by different metals and counter ions were transferred sensitively to the supramolecular level, observed by proportionate changes in the degree of twisting. Modification of the oxidation state of the metal center also gave large changes in twisting power; this suggests potential application in electrochemical molecular switches. The handedness of the induced cholesteric phase is related to the stereochemistry of the ligand: The small amount of chiral dopant needed for the LC technique (less than 2 nmol) suggests the possible determination of the absolute configuration of the parent primary amines of the ligands.

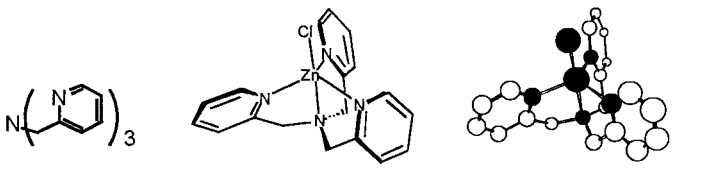
Keywords: chirality · circular dichroism · coordination chemistry · liquid crystals · supramolecular chemistry

Introduction

The structure (and symmetry) of liquid crystals arises from the balance of noncovalent inter- and intramolecular interactions involving small amounts of energy.[1] This implies that liquid crystalline materials are highly sensitive to chiral perturbation. It is well known, in fact, that doping a nematic phase with a nonracemic chiral compound induces the formation of a cholesteric phase:[2] The chiral information is transferred from the solute molecules to the bulk solvent and amplified. This amplification process has been extensively used for solving stereochemical problems[3] in which information on conformation or configuration of the dopant are obtained from studying the stereochemistry of the induced cholesteric phase. Furthermore, this phenomenon allowed the detection of small amounts of chiral nonracemic compounds.[4, 5]

Here we report that tripodal tetradentate ligands may act as chemosensor molecules: Their ability to twist a nematic phase increases upon copper ion complexation. The molecular chirality is transferred first from the molecular to supramolecular level and then the chiral shape of the complex is sensed by the nematic solvent. Furthermore, the value of the twisting power depends critically on the chiral shape of the complexes. We discuss here the discrimination of the different oxidation states of copper metal centers in connection with the different ligand conformations in the complex. This observation opens the road to possible electrochemical molecular switches that may find applications in the LC-display technology. Finally, the cholesteric induction may be used as a tool for assigning the absolute configuration of the ligands and hence of their parent primary amines.

In earlier investigations with the tris[(2-pyridyl)methyl]-amine (TPA, **1**) family of ligands,[6, 7] we observed in crystallographic structures of Zn^{II} and Cu^{II} complexes a distinct twist of the pyridine rings. That is, the planes of the pyridine rings were always tilted with respect to the central axis (N-Zn-Cl in Figure 1) of the molecule, which results in propeller-like structures.



TPA (**1**) [Zn(TPA)Cl]$^+$ [Zn(TPA)Cl]$^+$, X-ray[18]

Figure 1. Ligand TPA, and typical complexes.

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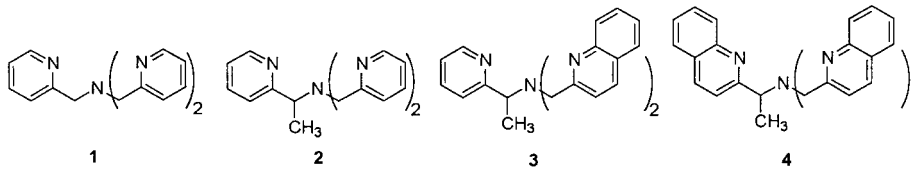
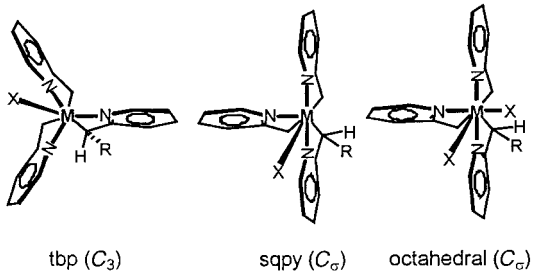
We found that it was possible to bias the helical twist by incorporation of a substituent in one of the CH_2 groups of the ligand, creating a chirality center (e.g. **2**). We showed that this chirality center dictates the handedness of the propeller-like helicity of the pyridine moieties in compounds **2**–**4**.[7, 8]



1 **2** **3** **4**

The compounds were characterized in the solid state by X-ray crystallography and in solution by circular dichroism (CD).[7] Similar observations were made for a series of related compounds.[8] From the CD spectra of the complexes we assigned the absolute sense of the orientation of the quinoline rings in solution.[9] Complexes of several metal ions were studied; it was found that only metals that bind the ligand in a trigonal bipyramidal coordination geometry (Zn^{II}, Cu^{II}) engendered a C_3-like conformation (Figure 2) in the ligand



tbp (C_3) sqpy (C_σ) octahedral (C_σ)

Figure 2. Conformations of ligands in trigonal bipyramidal (C_3), square pyramidal (C_σ), and octahedral (C_σ) metal ion coordination geometries.

and thus gave the propeller twist and large CD amplitudes. Metal ions forming octahedral complexes with **3** (Fe^{II}, Cd^{II}) enforced a distorted ligand conformation (C_σ, Figure 2), no twist, and low amplitude CD spectra. We utilized the conformation dependence of the chiroptical properties to the develop a "smart" chemosensor for metal ions based on CD and fluorescence spectroscopy.[10]

In this paper, we explore the twisting power of nematic liquid crystalline phases as a potential detection mechanism for metal ion sensors. In this first study, we shall focus on the issues of efficacy of twist induction and examine the potential sensitivity available by this technique.

Abstract in Italian: *Ligandi tetradentati tripodali possono agire da chemosensori; la loro capacità di trasformare una fase nematica in colesterica aumenta a seguito della complessazione con ioni rame. Inoltre le variazioni di forma dei complessi indotte dai diversi metalli e controioni sono state apprezzabilmente trasferite a livello supramolecolare e osservate attraverso le corrispondenti variazioni del grado di twist. Modifiche dello stato di ossidazione del centro metallico hanno portato a grosse variazioni di potere torcente suggerendo possibili applicazioni in dispositivi molecolari elettrochimici. Il senso del colesterico indotto è in relazione con la stereochimica del ligando: la piccola quantità di soluto chirale necessaria per la tecnica a cristalli liquidi (meno di 2 nmol) ne suggerisce il possibile uso nella determinazione della configurazione assoluta delle ammine primarie da cui i ligandi sono ottenuti.*

Results and Discussion

A series of coordination complexes of enantiomerically pure ligands **3**[6] and **4**[8] were prepared by precipitation methods. CD spectra of these complexes are shown in Figure 3 and Figure 4. The gross features of these spectra are consistent with those discussed with related, published complexes. While

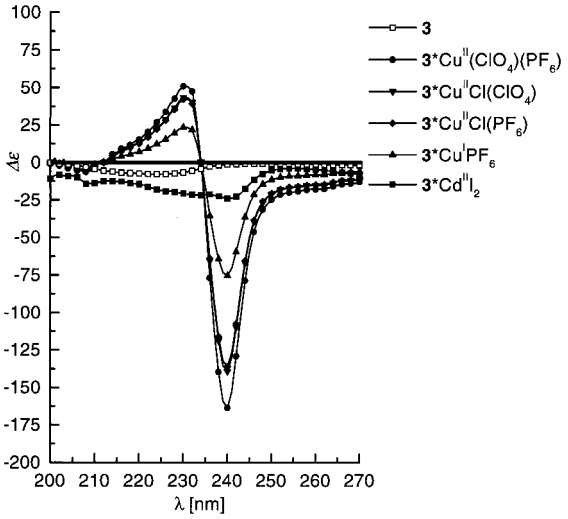


Figure 3. CD spectra of (*S*)-**3** and its Cu^{I}, Cu^{II}, and Cd^{II} complexes.

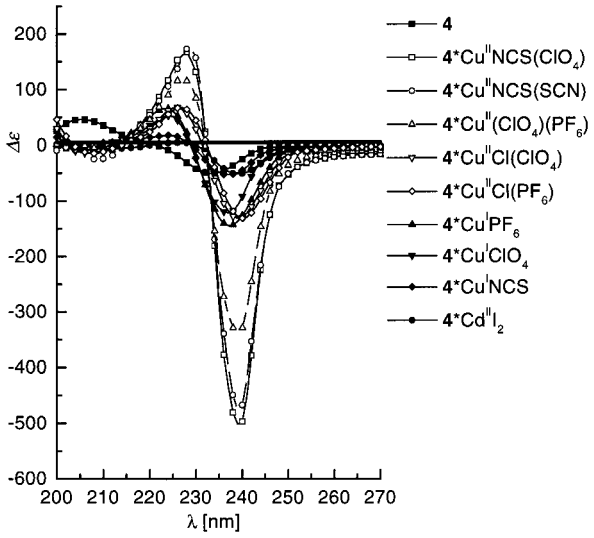


Figure 4. CD spectra of (*S*)-**4** and its Cu^{I}, Cu^{II}, and Cd^{II} complexes.

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the UV/Vis spectra in the 200–270 nm region are virtually identical for the free ligands and all of the complexes, the CD spectra differ markedly. The detailed analysis of the spectra will be discussed below.

The liquid crystal approach: A detailed investigation of the cholesteric induction requires the definition of the "helical twisting power" (i.e., the ability of a chiral dopant to twist a nematic phase).[5] This can be numerically expressed by β defined in Equation (1), where p is the cholesteric pitch, c the dopant molar fraction and r its enantiomeric excess.

$$\beta = (p \cdot c \cdot r)^{-1} \quad (1)$$

The sign of β is taken to be positive for a right-handed (P) induced cholesteric and negative for a left-handed (M) phase. From a stereochemical point of view, β characterizes a chiral dopant in a way similar to the classical rotatory power. Nevertheless, the origin of the two quantities is completely different. The optical rotation (as the other chiroptical quantities) is a consequence of the interaction between light and matter, while the cholesteric induction originates from a solute–solvent interaction. Reasonably, we can expect that the LC technique should be primarily sensitive to the molecular shape rather than to the electronic characteristics of the substituents present. The quantification of β requires the determination of the pitch and the sense of the cholesteric. This can be obtained with the nonspectroscopic Grandjean–Cano method.[11, 12]

The cholesteric induction phenomenon has been extensively used as a tool for assigning absolute configuration.[3] The approach may be simply correlative (when we compare the handedness of the cholesteric phase induced from the test molecule with that of analogous compounds of known configuration) or rational. In this latter case a model which relates the molecular chirality to the cholesteric chirality is required: The most successful model, originally proposed in 1983,[13] allows the determination of the configuration of binaphthyl (or more generally biaryl) atropoisomers.[3] More recently, a purely theoretical approach was proposed.[14]

Irrespective of the approach adopted, a reliable method requires relatively high twisting power ($>10\,\mu m^{-1}$). A prerequisite that a molecule must possess in order to show high twisting power is the presence of at least two planar (or *quasi*-planar) molecular fragments chirally twisted one with respect to the other in a relatively rigid conformation. In particular, *P*-skewed aromatic groups generate right-handed (P) cholesteric as a consequence of the transfer of chirality from the dopant to the bulk of the solvent through the chiral conformation of the latter.[3]

The free ligands: The helical twisting power of the two free ligands **3** and **4** in the nematic MBBA are relatively small (1–6 μm^{-1}), as expected for very flexible molecules.[3] The result parallels observations made by CD spectroscopy, where the free ligands show spectral amplitudes typical of heteroaromatic compounds with attached chirality centers.[6] This low propensity to torque the nematic phase implies that different LCs can exert different stabilization on molecular conformations modifying the actual conformation and/or the solute alignment leading to different handed cholesterics. Indeed, compound **4** shows twisting powers of almost the same small absolute value but opposite sign in the two solvents MBBA and E7.

The induction experiments were also carried out in E7. In general, similar trends with lower magnitudes were observed. Solubility of some complexes was lower in E7.

Complexes of 3: When ligand **3** is complexed with Cu^{I} or Cu^{II} ions, the twisting power increases by about 50 times (up to 98 μm^{-1}). This effect is a consequence of a) the molecular reorganization due to complexation that reduces the conformational mobility of **3** and b) the transfer of the chirality from the molecular level to the supramolecular arrangement. The large increase in twisting power correlates with the large increases in amplitude of the chiroptical properties of the complexes when studied in solution.[7] Both the solution and LC data are consistent with the conformationally flexible ligand which wraps around the metal ion and forms a geometrically defined, highly chiral structure in the complex. The structure of the related complex $[Cu^{II}((R)\text{-}\mathbf{3})(CH_3CN)](O_2CF_3)_2$ was previously established by X-ray crystallography (Figure 5), circular dichroism, UV/Vis spectroscopy, and elemental analysis.[9] The complex showed a trigonal bipyramidal (tbp) coordination geometry for the metal ion in the solid state; the solution spectra were consistent with this assignment. When the metal ion is tbp, the ligand adopts a C_3 conformation, which orients the two quinoline moieties in a highly asymmetric manner, with projection angle of $+12^{\circ}$. The (*R*)-**3** ligand displays a left-handed (Λ) helical chirality for the orientations of the planes of the heterocycles.

From inspection of Table 1, we notice that Cu^{I} (and Cu^{II}) complexes of the *S*-configured ligand **3** induces a left-handed (M) cholesteric. This chiral transfer (ligand to solvent organization) is mediated by the configuration around the metal center. In fact, the above-mentioned data as well as semi-empirical calculations of $[Cu^{II}((S)\text{-}\mathbf{3})Cl]^{+}$ indicate that

Table 1. Helical twisting powers β and g factors of (*S*)-**3** and (*S*)-**4** and of their Cu^{I}, Cu^{II}, and Cd^{II} complexes.

Dopant	β (SD) in MBBA	g ($\Delta\varepsilon/\varepsilon$, $\times 10^3$) in MeOH
3	n.d.[a]	0.01
3·$Cu^{II}(ClO_4)(PF_6)$	−98 (9)	5.60
3·$Cu^{II}Cl(ClO_4)$	−59.1 (8)	3.70
3·$Cu^{II}Cl(PF_6)$	−65 (3)	3.58
3·$Cu^{I}PF_6$	−65 (4)	2.20
3·$Cd^{II}I_2$	−12.9 (0.7)	0.82
4[b]	+2.2 (0.2)	1.22
4·$Cu^{II}NCS(ClO_4)$	−28.3	9.10
4·$Cu^{II}NCS(SCN)$	−19.0 (1.7)	8.75
4·$Cu^{II}(ClO_4)(PF_6)$	−23.7 (0.3)	6.71
4·$Cu^{II}Cl(ClO_4)$	−14.5 (0.3)	3.90
4·$Cu^{II}Cl(PF_6)$	−6.5 (0.2)	3.78
4·$Cu^{I}PF_6$[b]	−67.0 (3)	2.68
4·$Cu^{I}ClO_4$	−48.0 (5)	1.95
4·$Cu^{I}NCS$	$\lvert<3\rvert$	1.01
4·$Cd^{II}I_2$	−2.6 (0.4)	1.36

[a] n.d.: not detectable; isotropic at low dopant concentration. [b] The enantiomer was measured.

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ligand **3**, with an *S* configuration of the chirality center at the α carbon, would display a Δ (right-handed) propeller-like twist (see Figure 5). The correlation between the Δ configuration of the complex and the *M* handedness of the cholesteric was already described for the tris(pentane-2,4-dionate)metal(III)

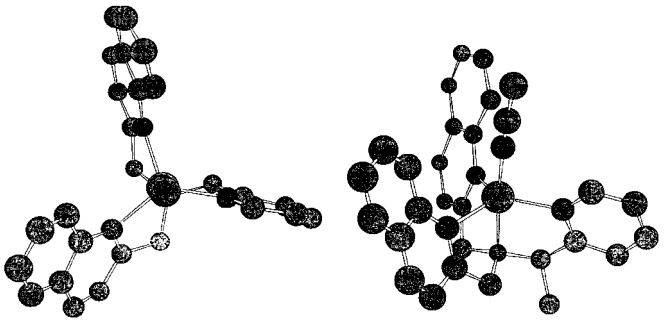

Figure 5. Top and side views of crystallographic structure of [Cu(**3**)-(CH_3CN)]$(O_2CF_3)_2$.[9]

C_3 complex[15, 16] and rationalized in terms of a molecular model similar to that proposed for biaryls.[13] In the three-bladed propeller, only two blades at a time can interact (and twist) the liquid crystalline host. For a Δ configuration, the spatial relationship between any pairs of blades has the same handedness of an *M*-biaryl (this same approach was used to interpret the excitonic CD spectra of the complexes);[9] accordingly, a Δ configuration may be associated with a left-handed (*M*) cholesteric.

As shown in Figure 6, we noted a correlation between the magnitude of β and the *g* factor (ratio of anisotropic and isotropic extinction coefficients, also called the anisotropy or

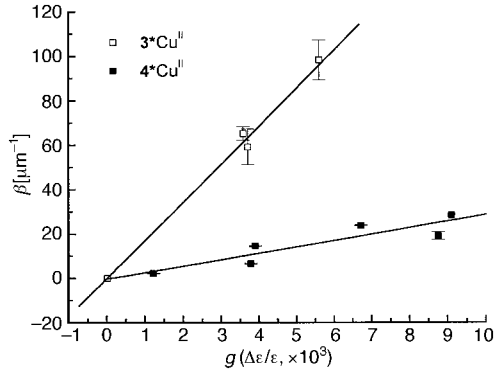

Figure 6. Graphical correlation of *g* against β for **3**·Cu^{II} and **4**·Cu^{II} complexes.

dissymmetry factor[17]). For the series of Cu^{II} complexes of **3**, the correlation between β and *g* is very strong as the counter ion is changed. Thus, factors that affect the *g* factor also appear to affect the helical twisting power. The counterions ClO_4^- and PF_6^- are weakly or noncoordinating, while Cl^- is more strongly coordinating, and distorts the complex as to reduce both *g* and β.

Since they are based on fundamentally different phenomena, why should β and *g* correlate with one another in this system? Both numbers are related, in part, to the dihedral angle between the planes of the chromophores, or in other words, to the overall "twist" of the ligand in the complex. This was already mentioned in the discussion of β. As the CD spectra of the Cu^{II} complexes of **3** can be described using the coupled oscillator model,[9] the spectral amplitude should vary with interchromophore dihedral angle. However, this angle is not the only factor that affects these parameters, as illustrated by the fact that the slopes of the line generated by complexes of **3** and **4** are quite different. The transfer of chirality from complex to the solvent is likely to be different in the two complexes, resulting in different slopes. The Cu^{I} complex also displayed a fairly high β.

To test the important role of the ligand conformation in determination of the value of β further, we measured the twisting power of the Cd^{II} complex with **3**. This metal ion is known to form six coordinate, octahedral complexes with related ligands.[18] Such metal ion geometry induces a C_σ conformation, which would not produce the propeller-like asymmetry which is also expressed by the low *g* factor (0.82).

Complexes of 4: The Cu^{II} complexes of **4** gave β values only 3–14 times greater than that of the free ligand. Similar to the Cu^{II} complexes of **3**, a linear relationship between the *g* factor and the helical twisting power was observed (Figure 6). However, the slope is far less steep, which results from both larger *g* numbers and smaller βs than observed for analogous complexes of **3**. Larger *g* numbers are observed due to the presence of three pairwise, additive interactions between the three quinoline chromophores,[8] while in **3** a maximum of one interaction is possible. The most likely explanation for the smaller β values is that Cu^{II} complexes of **4** transfer chiral information to the nematic solvent less efficiently. Complexes of **4** with Cu^{II} that give large β and *g* values are those that favor tbp coordination geometry for the metal (and thus C_3 conformation of the ligand) as judged by spectroscopic analysis of the d–d transitions.[8] Thus, even though CD and other data suggest that the NCS^- containing complexes have highly, anisotropic, pseudo-C_3 symmetry, their βs are not even half the size of the corresponding **3**·Cu^{II} complexes. The Cu^{II} complexes featuring no thiocyanate were found to adopt preponderant square pyramidal like structure, which leads to lower *g* factor and β value. This geometry does not enforce strongly achiral orientations of the heterocycle rings, so that the symmetry is broken only by the small perturbation exerted by the stereogenic center. The shape does not show, in this case, the feature of a chiral propeller whose presence is responsible for the high β values of copper complexes of **3**. The **4**·CdI_2 complex, was studied as a control experiment since the expected octahedral geometry would not produce the propeller-like asymmetry which is also reflected in the very low *g* factor (1.36). As expected a β value similar in magnitude to that of the free ligand **4** could be found.

Complexation of ligand **4** with Cu^{I}, in the absence of thiocyanate, lead to high twisting power, similar in magnitude to those observed for the complexes of **3** and much higher compared with Cu^{II} complexes of **4**. The similar twisting power of **4**·$Cu^{I}PF_6$ and **3**·$Cu^{I}PF_6$ suggests that only two blades are needed for the induction of a cholesteric mesophase if the dopant features a C_3 propeller-like structure.

Interestingly NCS^- greatly diminishes both β and g in **4**·$Cu^{I}NCS$. If thiocyanate is employed the C_3 symmetry vanishes. In this complex, one quinoline donor is decoordinated, with the thiocyanate is strongly bound to the copper center leading to a distorted structural arrangement.[8] In fact the β obtained in E7 was -3.5 and in MBBA $|<3|$ which is quite different from the other Cu^{I} complexes investigated.

General comments: The measurements of β are quite sensitive, requiring as little as 2 nmol of material for complexes with twisting powers in the order of 50, as shown by many of the present complexes. With miniaturization and device engineering, one might expect even lower detectable limits. These levels of detection suggest potential for further development of metal ion sensors[10] or further enhancements in detectability of absolute configurations of primary amines.[19]

Conclusion

The sensitivity of liquid crystals to chiral perturbations has been exploited to detect the different symmetry complexes obtained from tripodal tetradentate ligands **3** and **4** and Cu^+ and Cu^{2+} ions. Modification of the oxidation state of the metal ion in the complexes can significantly alter the twisting power of the complex; this suggests potential applications in the development of electrochiral liquid crystalline materials, possibly with attractive features such as low power consumption and bistability. Selection of counterion and ligand allows control of the observed twist. The correlation between g and β draws attention to common factors that affect these two seemingly disparate parameters, yet the differences observed emphasizes and clarifies the critical role that transfer of chiral information from the dopant to the nematic solvent plays in the overall twist induction phenomenon.

The pronounced difference between the metal ion complexes and the free ligands combined with high sensitivity suggests possible applications to metal ion sensors. Indeed, the intense twist induced by the complexes **3**·Cu^{2+}, the relative ease of synthesis of the ligand **3**, the small amount of chiral compound needed for the LC technique (less than 2 nmol) support this notion as well as the possibility of determination of the absolute configuration of primary amines.

Experimental Section

All reagents and solvents were purchased from commercial sources and used as received unless noted otherwise. The ligands **3** and **4** were prepared as reported previously.[8, 9] The following were distilled under nitrogen before use: diethyl ether from sodium/benzophenone and methylene chloride from CaH_2. Melting points were obtained with a MEL-TEMP II apparatus and are uncorrected. CD spectra were recorded on an AVIV 202 SF spectropolarimeter. CD and UV/Vis spectra were recorded in methanol.

General procedure for the pitch measurement: Cholesteric pitch values and helical handednesses were obtained utilizing the lens version[20] of the Grandjean–Cano method[1, 12] using a standard 16 Zeiss microscope equipped with a digital videocamera at room temperature. Cholesteric solution were prepared by dissolving the chiral solute in the nematic solvent MBBA (*N*-(4-methoxybenzilidene)-4-butylaniline) or E7 (eutectic mixture from Merck of 4-cyano-4′-pentyl/-heptyl/-octyloxy biphenyl and 4-cyano-4′-(4″-pentylphenyl) biphenyl). In a typical experiment, 20 mg of a solution containing about 1 nmol mg^{-1} of chiral dopant were used, the detectable limit of each cholesteric induction experiment is, in the most favorable cases, less than 2 nmol of complex.

Complex 3·$Cu^{II}(ClO_4)(PF_6)$: (**Caution!** *Perchlorate salts of metal complexes with organic ligands are potentially explosive. They should be handled in small quantity and with caution.*) A solution of $Cu(ClO_4)_2\cdot 6H_2O$ (185 mg, 0.5 mmol) in methanol (5 mL) was added through a pipet to a solution of **3** (200 mg, 0.5 mmol) in methanol (10 mL). After stirring for about 10 min, a solution of $NaPF_6$ (416 mg, 2.5 mmol) in methanol (5 mL) was added. A precipiate started to form upon addition of diethyl ether and was collected after 1 h stirring. The solid was washed with plenty of diethyl ether and dried to yield the title compound (210 mg, 60 %). M.p. 180 °C (decomp.); UV/Vis: λ (ε) = 233 (69 500 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{27}H_{24}N_4CuClO_4PF_6$: C 45.51, H 3.39, N 7.86; found: C 45.32, H 3.54, N 7.79.

Complex 3·$Cu^{II}Cl(ClO_4)$: A solution of $Cu(ClO_4)_2\cdot 6H_2O$ (97.6 mg, 0.263 mmol) in MeOH (2 mL) was added through a pipet to a solution of **3** (107 mg, 0.263 mmol) in methanol (10 mL). After the reaction mixture was stirred for about 10 min, a solution of NaCl (15.4 mg, 0.263 mmol) in H_2O (2 mL) was added. A precipitate formed immediately. The product was filtered, washed with diethyl ether and dried in vacuo to yield the title compound (90 mg, 56 %). M.p. 205 °C (decomp.); UV/Vis: λ (ε) = 232 (68 800 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{27}H_{24}N_4CuCl_2O_4$: C 53.78, H 4.01, N 9.29; found: C 53.79, H 3.84, N 9.48.

Complex 3·$Cu^{II}Cl(PF_6)$: Ligand **3** (200 mg, 0.5 mmol) and $CuCl_2\cdot 2H_2O$ (90 mg, 0.53 mmol) were mixed in methanol (15 mL). The solution was stirred at room temperature for 1 h and $NaPF_6$ (416 mg, 2.5 mmol) in methanol (5 mL) was added, whereupon a precipitate gradually formed. After the reaction mixture was stirred for a further 30 min, the solid was collected by filtration, washed with diethyl ether and dried in vacuo to yield the title compound (310 mg, 97 %). M.p. 196 °C (decomp.); UV/Vis: λ (ε) = 232 (68 300 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{27}H_{24}N_4CuClPF_6$: C 50.01, H 3.73, N 8.64; found: C 50.46, H 3.57, N 8.77.

Complex 3·$Cu^{I}PF_6$: Freshly distilled CH_2Cl_2 (10 mL) was added to **3** (110 mg, 0.27 mmol) and $[Cu(MeCN)_4]PF_6$ (100 mg, 0.27 mmol) in an inert glovebox. The solids gradually dissolved, and the solution became yellow. The yellow solution was allowed to stir for 15 min. Diethyl ether (50 mL) was used to precipitate a yellow solid. After filtration, the solid was washed with diethyl ether and dried under vacuum, resulting in 142 mg (85.5 %) of the yellow product. m.p. 191 °C (decomp.); UV/Vis: λ (ε) = 231 (68 600 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{27}H_{24}N_4CuPF_6$: C 52.9, H 3.94, N 9.13; found: C 52.78, H 3.95, N 9.08.

Complex 3·$Cd^{II}I_2$: A solution of CdI_2 (70 mg, 0.19 mmol) in methanol (2 mL) was added dropwise through a pipet to a warm solution of **3** (78 mg, 0.19 mmol) in methanol (5 mL). Upon cooling, a white precipitate formed at room temperature. The precipitate was collected, washed with methanol and dried in vacuo to yield a white powder (108 mg, 73 %). M.p. 165 °C (decomp.); UV/Vis: λ (ε) = 231 (61 600 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{27}H_{24}N_4CdI_2$: C 42.07, H 3.13, N 7.27; found: C 41.92, H 3.11, N 7.23.

Complex 4·$Cu^{II}NCS(ClO_4)$: A solution of $Cu(ClO_4)_2\cdot 6H_2O$ (81.5 mg, 0.22 mmol) in methanol (2 mL) was added through pipet to a solution of **4** (100 mg, 0.22 mmol) in methanol (10 mL). After the solution was stirred for about 10 min, a solution of KSCN (21 mg, 0.216 mmol) in methanol (1 mL) was added. A precipiate started to form immediately and was collected after 1 h stirring. The solid was washed with plenty of diethyl ether and dried to yield the title compound (124 mg, 83.3 %). M.p. 162 °C (decomp.); UV/Vis: λ (ε) = 232 (124 000 mol^{-1} dm^3 cm^{-1}); elemental analysis calcd (%) for $C_{32}H_{26}N_5CuClO_4S$: C 56.88, H 3.87, N 10.36; found: C 56.82, H 3.74, N 10.06.

Complex 4·$Cu^{II}NCS(SCN)$: Ligand **4** (200 mg, 0.44 mmol) and $CuCl_2\cdot 2H_2O$ (75 mg, 0.44 mmol) were added to methanol (3 mL). The solution was stirred at room temperature for 1 h and KSCN (128 mg, 1.3 mmol) in methanol (2 mL) was added, whereupon a precipitate gradually formed. After the reaction mixture was stirred for 30 min the solid was collected by filtration, washed with methanol and dried in vacuo to yield the title compound (250 mg, 90 %). M.p. 116 °C (decomp.); UV/Vis: λ (ε) = 230

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($128\,000\ mol^{-1}\,dm^3\,cm^{-1}$); elemental analysis calcd (%) for $C_{33}H_{26}N_6CuS_2$: C 62.49, H 4.13, N 13.25; found: C 62.28, H 3.98, N 13.39.

Complex 4·Cu^{II}(ClO$_4$)(PF$_6$): A solution of $Cu(ClO_4)_2\cdot 6H_2O$ (162 mg, 0.438 mmol) in methanol (10 mL) was added through pipet to a solution of **4** (200 mg, 0.44 mmol) in methanol (20 mL). After the reaction mixture was stirred for about 10 min, a solution of $NaPF_6$ (367 mg, 2.2 mmol) in methanol (8 mL) was added. A precipiate started to form immediately and was collected after 1 h stirring. The solid was washed with plenty of diethyl ether and dried to yield the title compound (287.8 mg, 86.2 %). M.p. 200 °C (decomp.); UV/Vis: λ (ε) = 231 ($116\,000\ mol^{-1}\,dm^3\,cm^{-1}$); elemental analysis calcd (%) for $C_{31}H_{26}N_4CuClO_4PF_6$: C 48.83, H 3.43, N 7.35; found: C 49.10, H 3.61, N 7.34.

Complex 4·Cu^{II}Cl(ClO$_4$): A solution of $Cu(ClO_4)_2\cdot 6H_2O$ (73.8 mg, 0.2 mmol) in MeOH (1 mL) was added through a pipet to a solution of **4** (91 mg, 0.2 mmol) in methanol (5 mL). After the reaction mixture was stirred for about 10 min, a solution of NaCl (11.7 mg, 0.2 mmol) in H_2O (0.5 mL) was added. A precipitate formed immediately. The product was filtered, washed with diethyl ether and dried in vacuo to yield the complex (64 mg, 49 %). M.p. 182 °C (decomp.); UV/Vis: λ (ε) = 231 ($113\,000\ mol^{-1}\,dm^3\,cm^{-1}$); elemental analysis calcd (%) for $C_{31}H_{26}N_4CuCl_2O_4$: C 57.02, H 4.01, N 8.57; found: C 56.98, H 3.97, N 8.58

Complex 4·Cu^{II}Cl(PF$_6$): Ligand **4** (100 mg, 0.22 mmol) and $CuCl_2\cdot 2H_2O$ (29.5 mg, 0.22 mmol) were mixed in methanol (15 mL). The solution was allowed to stir at room temperature for 1 h and $NaPF_6$ (184 mg, 1.1 mmol) in methanol (3 mL) was added, whereupon a precipitate gradually formed. After the reaction mixture was stirred for 30 min the solid was collected by filtration, washed with diethyl ether and dried in vacuo to yield the title compound (133.1 mg, 87 %). M.p. 180 °C (decomp.); UV/Vis: λ (ε) = 231 ($115\,000\ mol^{-1}\,dm^3\,cm^{-1}$); elemental analysis calcd (%) for $C_{31}H_{26}N_4CuClPF_6$: C 53.30, H 3.75, N 8.02; found: C 53.47, H 3.77, N 8.01.

Complex 4·Cu^{I}PF$_6$: Freshly distilled CH_2Cl_2 (10 mL) was added to **4** (100 mg, 0.22 mmol) and $[Cu(MeCN)_4]PF_6$ (80 mg, 0.21 mmol) in an inert glovebox. The solids gradually dissolved, and the solution turned yellow. The yellow solution was stirred for 15 min. Diethyl ether (50 mL) was used to precipitate a yellow solid. After filtration the solid was washed with diethyl ether and dried under vacuum, resulting in the yellow product (114.4 mg, 78.4 %). M.p. 198 °C (decomp.); UV/Vis: λ (ε) = 230 (100 000); elemental analysis calcd (%) for $C_{31}H_{26}N_4CuPF_6$: C 56.15, H 3.95, N 8.45; found: C 55.91, H 3.75, N 8.35.

Complex 4·Cu^{I}ClO$_4$: Freshly distilled CH_2Cl_2 (15 mL) was added to **4** (200 mg, 0.44 mmol) and $[Cu(MeCN)_4]ClO_4$ (142 mg, 0.434 mmol) in an inert glovebox. The solids gradually dissolved, and the solution turned yellow. The yellow solution was stirred for 15 min. Diethyl ether (70 mL) was used to precipitate a yellow solid. After filtration the solid was washed with diethyl ether and dried under vacuum, resulting in the yellow product (260 mg, 96 %). M.p. 175 °C (decomp.); UV/Vis: λ (ε) = 230 (101 000); elemental analysis calcd (%) for $C_{31}H_{26}N_4CuClO_4$: C 60.29, H 4.24, N 9.07; found: C 60.23, H 4.21, N 9.01.

Complex 4·Cu^{I}NCS: A suspension of CuSCN (27 mg, 0.223 mmol) in cold dimethylsulfoxide (2 mL) was added to a hot solution of **4** (100 mg, 0.22 mmol) in dimethylsulfoxide (3 mL). The solution gradually turned clearer and was stirred for 30 min. After the solution was evaporated to dryness the remaining solid was taken up in CH_2Cl_2 (10 mL). Diethyl ether (40 mL) was used to precipitate a yellow solid. After filtration, the solid was washed with diethyl ether and dried under vacuum, resulting in the yellow product (92 mg, 73 %). M.p. 130 °C (decomp.); UV/Vis: λ (ε) = 231 (120 000); elemental analysis calcd (%) for $C_{32}H_{26}N_5CuS$: C 66.70, H 4.55, N 12.15; found: C 66.91, H 4.48, N 12.35.

Complex 4·Cd^{II}I$_2$: A solution of CdI_2 (307 mg, 0.839 mmol) in methanol (10 mL) was added dropwise through a pipet to a warm solution of **4** (380 mg, 0.837 mmol) in methanol (50 mL). Upon cooling, a white precipitate formed at room temperature. The precipitate was collected, washed with methanol and dried in vacuo to yield a white powder (600 mg, 87 %). M.p. 170 °C (decomp.); UV/Vis: λ (ε) = 231 (95 300); elemental analysis calcd (%) for $C_{31}H_{26}N_4CdI_2$: C 45.36, H 3.19, N 6.82; found: C 45.32, H 3.11, N 6.73.

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