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A Fluorescent Dissymmetric Thiosemicarbazone Ligand Containing a Hydrazonequinoline Arm and Its Complexes with Cadmium and Mercury

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A new dissymmetric thiosemicarbazone ligand containing a hydrazonequinoline arm, H_2AMeTsQ, and its chloride salt, [H_3AMeTsQ]Cl, were synthesized. Nine new complexes of cadmium and mercury with different structural characteristics were obtained under different reaction conditions as the ligand charge can be controlled by varying the amount of base. ^{113}Cd and ^{199}Hg NMR spectroscopy together with X-ray diffraction indicated that the complexes form monomeric and dimeric structures and even a coordination polymer. Fluorescence spectroscopy showed that both protonated and neutral forms of the ligand were fluorescent as well as some of their cadmium and mercury derivatives. The fluorescence intensity decreased upon complexation and in some complexes a shift of the emission maximum was also observed.

Introduction

The synthesis of organic compounds with a large number of donor atoms has acquired special relevance in recent years owing to their relationship with biological systems and their ability to detect and remove metals harmful to humans and the environment.[1–4] Within this group, the thiosemicarbazones (TSCs) are ligands of great interest because of their versatility as donor systems, the variety of chemical species that can result,[5] the wide and important types of reaction they can undergo, and their biological, structural and optical properties.[6–10] The design and synthesis of dissymmetric double-Schiff-base ligands containing this TSC moiety started during the last decade, but only few research groups have developed efficient strategies as the accessibility of such dissymmetric ligands is often hampered by several synthetic problems. The problems found in the synthesis include ring-closure reactions or the obtainment of the corresponding symmetric ligands, as well as ligand mixtures that are very difficult to purify.[11–13] However, dissymmetric TSCs open the possibility of a greater range of donor atoms and allow the properties of metal complexes to be finely tuned for a variety of possible applications.[14–17] Complexes with copper have been explored as imaging agents in positron emission tomography (PET) studies to identify hypoxic tissues.[17–20] Recently, a bis(thiosemicarbazonate)copper(II) complex has been proposed to be of use as a copper-64 radiopharmaceutical to assist in the diagnosis of Alzheimer's disease,[21] and fluorescent and biocompatible aromatic Ga^{III} and In^{III} bis(thiosemicarbazonato) complexes for dual mode optical and PET or SPECT (single-photon emission computed tomography) molecular imaging have been synthesized.[22]

In recent years, there has been growing interest in compounds that can form selective and stable complexes with cadmium and mercury to remove or to detect them.[23,24] Some thiosemicarbazones show high selectivity for specific metal ions,[25,26] so it could be expected that dissymmetric ligands derived from thiosemicarbazides would be suitable molecules for these purposes as they form stable tetradentate chelates. The addition of a fluorophore allows the synthesis of fluorescent molecules. The fluorescence can be increased by the dissymmetry of the ligands, which makes them suitable as precursors of luminescent or redox sensors.[27–29]

On the other hand, the use of established fluorescence tags as pendant fluorophores attached to some Zn^{II} bis(thiosemicarbazonate) systems is likely to significantly perturb the distribution of the probe.[26,30] Therefore, there is scope for designing small, intrinsically fluorescent molecules that could act as versatile dual mode optical and PET imaging probes. The higher intrinsic fluorescence coupled with solubility and stability in a biologically compatible medium should facilitate the monitoring of cell delivery and biodistribution in cancer cells. In particular, the fluorescence emission of some zinc(II) bis(thiosemicarbazonato)

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complexes has previously been used to follow cellular uptake and intracellular localization in a range of different cancer cell phenotypes.[31–33]

To better understand the behaviour of this new family of dissymmetric thiosemicarbazones, which match the requirements for cell labelling and/or chemical sensors for toxic metals, we report herein the coordination chemistry of a new hybrid ligand derived from 2-hydrazinoquinoline and 4-methyl-3-thiosemicarbazide (H_2AMeTsQ) and its chloride salt [H_3AMeTsQ]Cl with cadmium and mercury nitrates.

The new complexes were fully characterized by elemental analysis, IR spectroscopy, ^{1}H, ^{13}C, ^{113}Cd and ^{199}Hg NMR spectroscopy in solution and in the solid state, mass spectrometry, fluorescence spectroscopy and some of them by single-crystal X-ray diffraction.

Results and Discussion

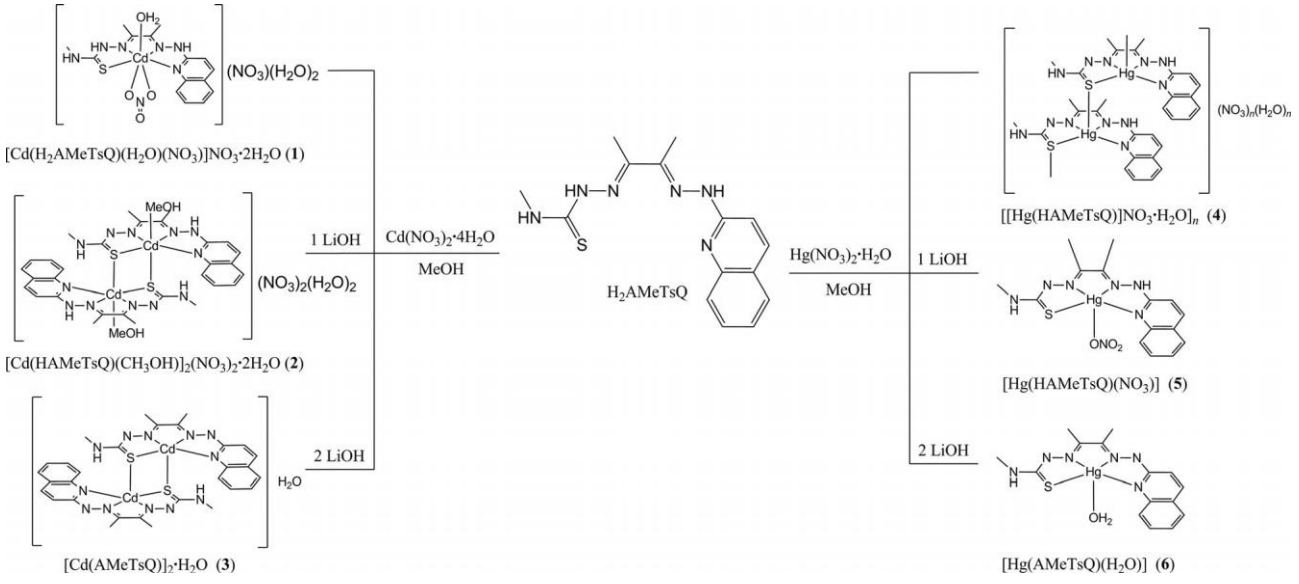
Synthesis

The absence or the presence of hydrochloric acid in the reaction medium allowed the isolation of the neutral ligand H_2AMeTsQ or its chloride salt [H_3AMeTsQ]Cl. The reactivity of both ligands was explored in methanol and in the presence of one or two equivalents of lithium hydroxide for H_2AMeTsQ and for [H_3AMeTsQ]Cl, which has three acidic hydrogen atoms, three equivalents of base were also used. All the complexes showed a 1:1 ligand-to-metal stoichiometry, although their composition and structure depend on the reaction conditions, in particular in the amount of base used (Schemes 1 and 2), as the ligand can behave as a neutral, singly or doubly deprotonated donor. Thus, the synthesis without LiOH·H_2O, or with one equivalent when [H_3AMeTsQ]Cl was used, led to the formation of complexes containing two nitrate groups, and therefore a neutral ligand (**1** and **9**), except the polymeric mercury complex **4**, in which the ligand was spontaneously singly deprotonated. In most cases, the ligand charge could be controlled by addition of the appropriate amount of base owing to the different acidity of the NH groups. In the reactions of H_2AMeTsQ with one or two moles of base, it was possible to isolate complexes with one NO_3^- group and a negatively charged ligand (**2** and **5**) or without NO_3^- with the ligand doubly deprotonated (**3** and **6**). In the reactions of [H_3AMeTsQ]Cl with one equivalent of base, **7** and **9**, which contain a neutral ligand, could be synthesized as the LiOH·H_2O removed the proton on the quinoline ring. Thus, with two equivalents of base a complex with one singly deprotonated ligand is obtained (**8**), whereas with three equivalents of base the ligand is doubly deprotonated to yield complexes **3** and **6**.

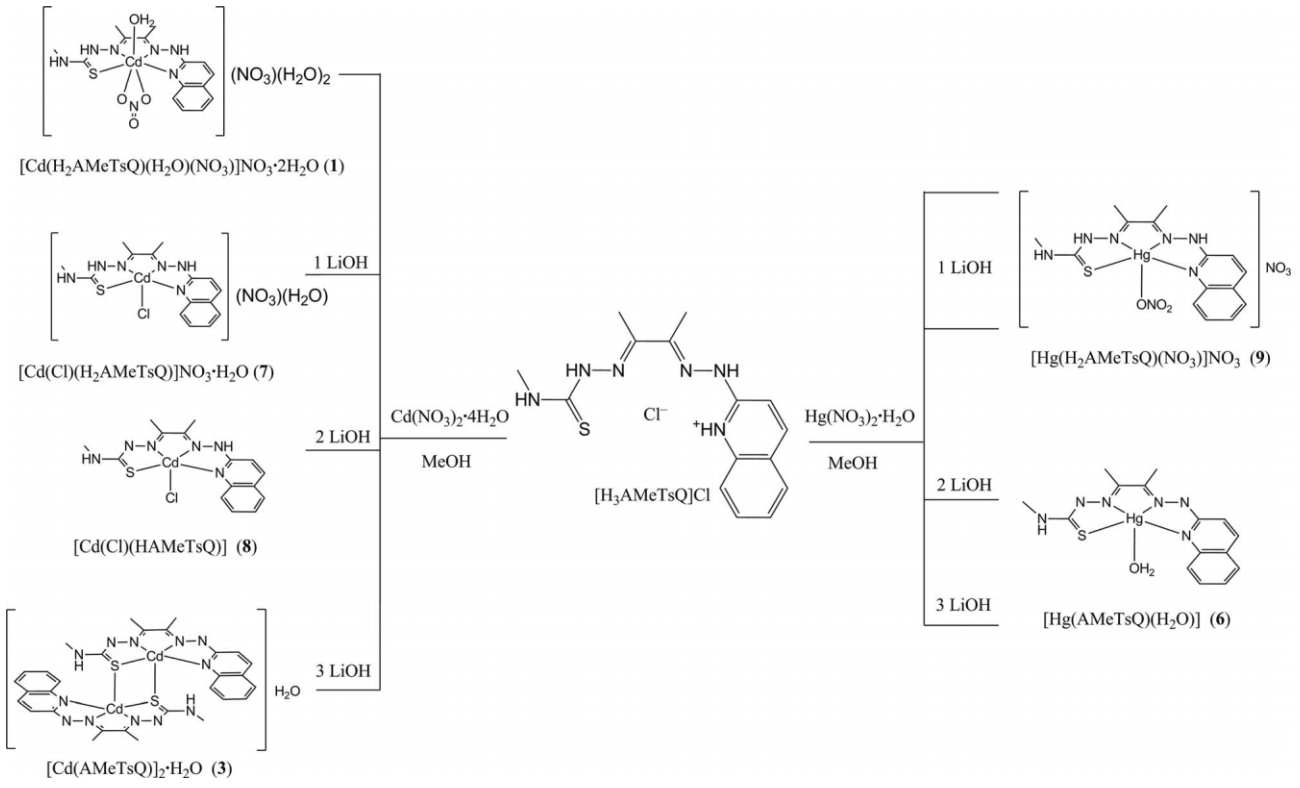
Conductivity measurements of **3**, **6** and **8** in *N*,*N*-dimethylformamide (DMF) showed that they are molecular species, whereas the values observed for **1**, **4**, **7** and **9** corresponded to 1:1 electrolytes and that for **2** was in the range expected for 2:1 electrolytes.[34] The value for **5**, which is relatively high for a molecular species, could suggest partial solvolysis of the coordinated NO_3^- group by DMF molecules. The mass spectra of all the complexes showed peaks corresponding to the ion $[M(HAMeTsQ)]^+$. In addition, in the spectrum of **2** the peak corresponding to the fragment $[Cd_2(HAMeTsQ)_2 + H]^+$ was observed, which suggests a dimeric structure. In all the complexes, the calculated and experimental isotopic splitting patterns were identical.

X-ray Analysis

The crystallographic and refinement data are summarized in Table 1. In all the complexes, the ligand behaved at least as a tetradentate N_3S chelate, a coordination mode that leads to the formation of three five-membered chelate rings that confer high stability to the compounds. The Sup-



Scheme 1. Proposed structures of complexes obtained from H_2AMeTsQ.



Scheme 2. Proposed structures of complexes obtained from [H3AMeTsQ]Cl.

Table 1. Crystal data and structure refinement for **1**, **2** and **4**·DMSO.

	1	**2**	**4**·DMSO
Formula	$C_{15}H_{24}CdN_8O_9S$	$C_{16}H_{23}Cd\ N_7O_5S$	$C_{17}H_{23}HgN_7O_5S_2$
Formula weight	604.88	537.87	670.13
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	Cc
a [Å]	9.5909(8)	9.3384(2)	15.460(2)
b [Å]	11.4287(11)	9.5141(3)	22.132(3)
c [Å]	11.8915(11)	12.7202(5)	7.5636(11)
α [°]	113.464(4)	102.125(2)	90
β [°]	94.039(5)	95.684(2)	117.775(7)
γ [°]	106.783(5)	106.123(2)	90
U [Å^3]	1118.93(18)	1046.47(6)	2289.8(5)
Z	2	2	4
D_c [Mg m^{-3}]	1.795	1.707	1.944
Absorption coefficient [mm^{-1}]	1.135	9.681	6.948
F(000)	612	544	1304
Goodness of fit on F^2	1.061	1.057	1.021
Reflections collected	31148	10626	32343
Independent reflections	4893 [R(int) = 0.0438]	3621 [R(int) = 0.0365]	6495 [R(int) = 0.0573]
Final R_1 and $wR_2[I > 2\sigma(I)]$	0.0273, 0.0616	0.0256, 0.0665	0.0277, 0.0630
Residual electron density (min./max.) [e Å^{-3}]	–0.457, 1.048	–0.719, 0.816	–1.572, 1.162

porting Information contains a table with the full bond lengths and angles as well as the hydrogen bonding information.

The crystal structure of **1** is made up of a $[Cd(H_2AMeTsQ)(H_2O)(NO_3)]^+$ cation, a nitrate group and two water molecules. In the cation, the cadmium is coordinated to a neutral tetradentate ligand, a bidentate NO_3^- group and a molecule of water, which results in a capped octahedral environment with the ligand in the equatorial plane (Figure 1). The ligand skeleton can be considered planar with a maximum deviation from the least-squares plane of 0.056 Å for C(2). The NO_3^- ion is coordinated in an asymmetric mode, with one of the Cd–O bond lengths much longer than the other (Table 2). There is an extended network of hydrogen bonds between the NO_3^- groups and the water molecules, which leads to a 3D architecture.

Complex **2** comprises the dimeric unit $[Cd(CH_3OH)(HAMeTsQ)]_2^{2+}$, two nitrate groups and two

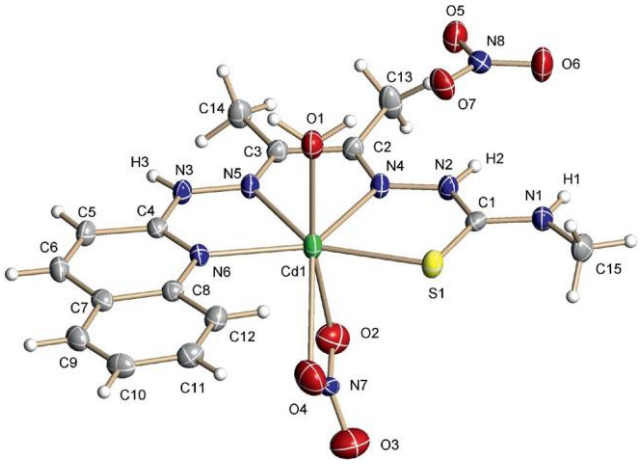


Figure 1. Molecular structure of **1**. The water molecules are omitted for clarity. Thermal ellipsoids at 50 % probability.

Table 2. Selected M–L bond lengths in **1**, **2** and **4**·DMSO.

	1	**2**	**4**·DMSO
M(1)–N(4)	2.385(2)	2.320(2)	2.440(11)
M(1)–N(5)	2.348(2)	2.335(2)	2.417(4)
M(1)–N(6)	2.2988(19)	2.3044(19)	2.278(4)
M(1)–S(1)	2.5410(7)	2.5411(6)	2.6458(11)
M(1)–S(1)#1	–	2.7356(6)	2.440(4)
M(1)–O(1)	2.406(2)	2.350(2)	–
M(1)–O(2)	2.435(2)	–	–
M(1)–O(4)	2.636(2)	–	–

water molecules (Figure 2). The cadmium ion is hexacoordinated by one monodeprotonated tetradentate ligand, one methanol molecule and the sulfur atom of a neighbouring ligand that bridges to another Cd atom. The Cd–S_{bridge} bond length is longer than the other Cd–S bond (Table 2). Deprotonation takes place in the thiosemicarbazone branch. The ligand is slightly buckled, and the sulfur atom is 0.29 Å above the least-squares plane defined by C(1)–N(2)–N(4)–C(2)–C(3)–N(5)–N(3)–C(4)–N(6). The cations, the water molecules and the nitrates are bonded through hydrogen bonds in the *ac* plane. These planes are linked by CH···C–H interactions between the quinoline rings, which gives rise to a 3D structure.

Complex **4** is made up of $[Hg(HAMeTsQ)]^+$ units, one nitrate group, a water molecule and a dimethyl sulfoxide (DMSO) molecule (Figure 3). In the cation, the mercury is coordinated to a tetradentate ligand and to the sulfur atom of a neighbouring ligand that bridges two metal centres. The metal is in a distorted square-base pyramid (sbp), with $\tau = 0.054$ ($\tau = 0$ for sbp and $\tau = 1$ for trigonal bipyramid, tbp).[35] The coordination mode of the ligand affords polymeric chains that run along the *c* axis. The nitrate group and the water molecule are bonded to the cations through hydrogen bonds with the NH groups. Although the hydrogen atoms of the water molecules could not be located, they clearly present short contacts with the DMSO molecule and with the NO_3^- ion, which suggests the presence of hydrogen bonds that link the polymeric chains to form sheets in the *ac* plane.

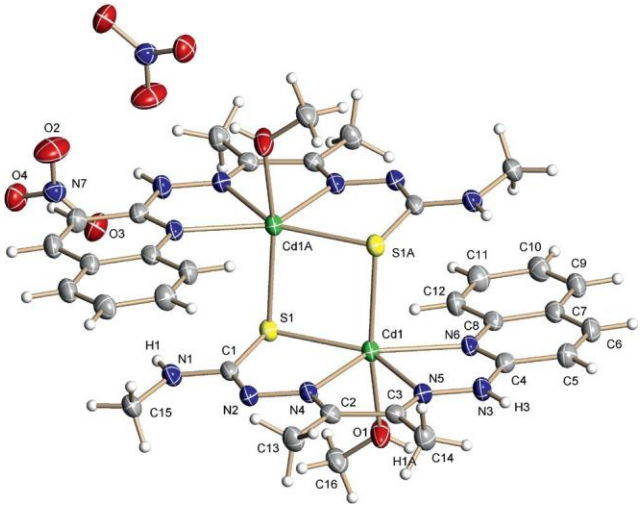


Figure 2. Molecular structure of **2**. The water molecules are omitted for clarity. Thermal ellipsoids at 50 % probability.

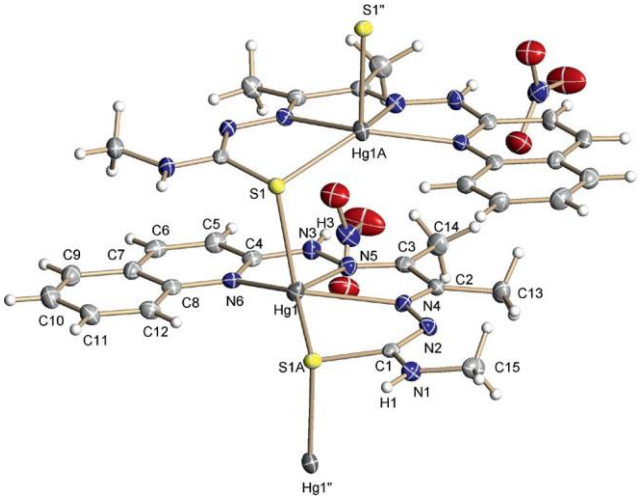


Figure 3. Molecular structure of **4**·DMSO. The water and DMSO molecules are omitted for clarity. Thermal ellipsoids at 50 % probability.

Spectroscopy

The spectroscopic data of the organic molecules confirm the formation of the new dissymmetric thiosemicarbazone ligands. In the IR spectra of all the complexes, coordination of the thioamide group to the metal was indicated by the shift of the ν(CS) band to lower frequencies compared to that of the free ligand. In contrast, the ν(CN) bands were almost in the same position, but the crystal structure determinations of **1**, **2** and **4** confirm coordination of a tetradentate N_3S ligand. This could be because thiosemicarbazones are extensively delocalized systems and the CN bond lengths are relatively unaffected by metal coordination. The spectra of **1**, **2**, **4**, **5**, **7** and **9** also showed bands at ca. 1385 cm^{-1} that confirmed the presence of NO_3^- groups.

In the ^1H NMR spectra of both forms (neutral and protonated) of the ligand, it could be observed that the formation of the chloride salt caused a greater deshielding of the

Table 3. Chemical shifts δ [ppm] and spin coupling constants J [Hz] observed in the ^{1}H NMR spectra of the ligands and the complexes in [D$_6$]DMSO.

	3-H	2-H	6-H, 6a-H[a]	1-H	9-H	5-H	11-H	12-H	10-H	15-H	13-H, 14-H	CH_3OH
H_2AMeTsQ	10.33, 1 H, s	10.14, 1 H, s	8.20, 1 H, d, ^3J = 8.8	8.31, 1 H, q, ^3J = 4.6	7.80, 1 H, d, ^3J = 7.9		7.70–7.55, 3 H, m		7.31, 1 H, t, ^3J = 7.3	3.04, 3 H, d, ^3J = 4.6	2.26, 6 H, s	–
[H_3AMeTsQ]Cl	12.28, 0.8 H, br. s	10.41, 1 H, s	8.55, 1 H, d, ^3J = 9.4; 13.03, 0.3 H, br. s	8.51, 1 H, q, ^3J = 4.4	8.01, 1 H, d, ^3J = 7.7	8.11, 1 H, br. s	7.85, 1 H, t, ^3J = 7.4	7.77, 1 H, d, ^3J = 9.4	7.57, 1 H, t, ^3J = 7.5	3.05, 3 H, d, ^3J = 4.5	2.45, 3 H, s; 2.39, 3 H, s	–
1	11.59, 1 H, br. s	10.33, 1 H, s	8.60–8.33, 2 H, m		8.08–7.88, 2 H, m		7.78, 1 H, t, ^3J = 7.5	7.57, 1 H, d, ^3J = 9.2	7.50, 1 H, t, ^3J = 7.3	3.05, 3 H, d, ^3J = 4.5	2.37, 3 H, s; 2.35, 3 H, s	–
2	11.54, 1 H, s	–	8.34, 1 H, d, ^3J = 9.0	7.54–7.43, 1 H, m	7.91, 1 H, d, ^3J = 7.6	7.29, 1 H, d, ^3J = 9.0	7.79, 1 H, ddd, ^4J = 1.3, ^3J = 7.2, ^3J = 8.3	7.54–7.43, 2 H, m		2.90, 3 H, d, ^3J = 2.7	2.36, 3 H, s; 2.32, 3 H, s	4.08, 1 H, q (OH), ^3J = 5.2; 3.16, 3 H, d (CH_3), ^3J = 5.2
3	–	–	7.69, 1 H, d, ^3J = 9.1	7.12–6.95, 1 H, m	7.52, 1 H, d, ^3J = 7.3	6.79, 1 H, d, ^3J = 9.1	7.43, 1 H, ddd, ^4J = 1.2, ^3J = 7.1, ^3J = 8.5	7.12–6.95, 2 H, m		2.85, 3 H, d, ^3J = 4.7	2.24, 3 H, s; 2.23, 3 H, s	–
4	12.12 1 H, s	–	8.46 1 H, d ^3J = 8.4	8.10–7.95 2 H, m		7.43 1 H, d ^3J = 8.9	7.93–7.45 2 H, m		7.54 1 H, t ^3J = 6.9	2.95 3 H, s	2.38 3 H, s; 2.31 3 H, s	–
5	12.06, 1 H, s	–	8.43, 1 H, d, ^3J = 9.0	7.91, 1 H, q, ^3J = 4.5	7.98, 1 H, d, ^3J = 7.8	7.42, 1 H, d, ^3J = 8.9	7.88–7.73, 2 H, m		7.52, 1 H, t, ^3J = 7.4	2.93, 3 H, d, ^3J = 4.5	2.37, 3 H, s; 2.31, 3 H, s	–
6	–	–	7.59, 1 H, d, ^3J = 10.5	7.45–7.33, 1 H, m	7.51, 1 H, d, ^3J = 6.7	6.75, 1 H, d, ^3J = 9.8	7.45–7.33, 1 H, m	7.26, 1 H, d, ^3J = 9.5	7.03, 1 H, t, ^3J = 6.5	2.88, 3 H, d, ^3J = 4.4	2.24, 3 H, s; 2.20, 3 H, s	–
7	10.39, 1 H, s	10.16, 1 H, s	8.21, 1 H, d, ^3J = 8.7	8.33, 1 H, q, ^3J = 4.1	7.81, 1 H, d, ^3J = 7.9		7.74–7.53, 3 H, m		7.33, 1 H, t, ^3J = 7.4	3.03, 3 H, d, ^3J = 4.5	2.27, 6 H, s	–
8	11.67, 1 H, br. s	–	8.26, 1 H, d, ^3J = 9.0	7.49–7.36, 1 H, m	7.87, 1 H, d, ^3J = 7.7	7.25, 1 H, d, ^3J = 9.0	7.72, 1 H, t, ^3J = 7.5	7.49–7.36, 2 H, m		2.89, 3 H, d, ^3J = 4.4	2.35, 3 H, s; 2.29, 3 H, s	–
9	11.99, 1 H, s	10.68, 1 H, s	8.48, 1 H, s	8.88, 1 H, s	7.98, 1 H, d, ^3J = 7.8	8.04, 1 H, s	7.82, 1 H, t, ^3J = 7.2	7.65–7.36, 2 H, m		3.02, 3 H, d, ^3J = 4.5	2.39, 6 H, s	–

[a] Only present in [H_3AMeTsQ]Cl.

majority of the hydrogen atoms (Table 3). The additional proton due to the protonation of the quinoline ring was not fully observed in [D$_6$]DMSO, probably because of an exchange with residual water molecules in the solvent. The ^{1}H NMR spectra of all the complexes confirmed the deprotonation state of the ligand as well as the loss of the hydrogen atom on the quinoline ring. The presence of two signals above 10 ppm, which correspond to the hydrogen atoms from the acidic amine groups, in the spectra of compounds **1**, **7** and **9** showed that the ligand was neutral. The spectra of **2**, **4**, **5** and **8** showed only the loss of the acidic hydrogen atom from the thiosemicarbazone portion of the ligand, which indicates that the ligand was singly deprotonated. The double deprotonation in **3** and **6** could be confirmed by the lack of any signal above 10 ppm.

In the ^{13}C NMR spectra of all the complexes, the signals corresponding to the CS and CN groups and the quinoline ring were shifted with respect to those of the free ligand, which indicates coordination through these groups. In the spectra of the mercury complexes, the shift of the CS signal

to lower field was considerably larger than in the cadmium derivatives, as could be expected, because the Hg–S bond is stronger than the Cd–S bond.

It is known that the ^{113}Cd chemical shift is very sensitive to changes in the coordination number of cadmium as well as to the nature of the bonding. Replacement of a sulfur atom by a nitrogen or oxygen atom tends to give greater shielding,[36–40] and a decrease in the coordination number tends to give greater deshielding.[41,42] The presence of only one signal in the spectra of all the complexes indicated only one type of chemical environment for the cadmium ion. In **1**, the signal was observed at δ = 122 ppm (–520 ppm vs. $CdMe_2$), which was in agreement with the N_3SO_3 environment found in the crystal structure. In **2**, the value was 250 ppm (–392 ppm vs. $CdMe_2$), which shows a lower coordination number and an increase in the number of sulfur atoms bound to the metal, as expected for the N_3S_2O environment confirmed by X-ray analysis (Figure 4). In the ^{113}Cd cross polarization magic angle spinning (CP/MAS) NMR spectra of **3**, **7** and **8**, signals at 441, 418 and 440 ppm, respectively, could be observed (Figure 5), which suggests that the cadmium ion in all three complexes has the same coordination number and that it is lower than that of **1** and **2**. In view of the data from the other techniques, a N_3S_2 coordination environment was proposed for **3** and a N_3SCl coordination environment for **7** and **8**. The spectrum of **3** in DMSO showed a signal at δ = 307 ppm (–335 ppm vs. $CdMe_2$), which indicates coordination of the solvent and therefore a higher coordination number.

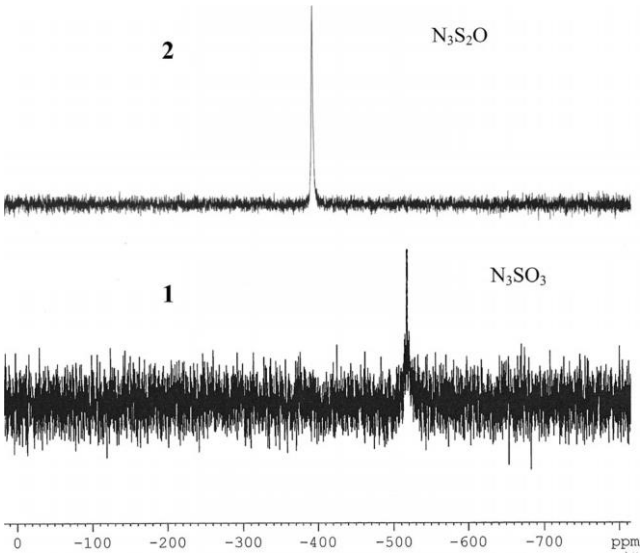


Figure 4. ^{113}Cd NMR spectra ([D$_6$]DMSO) of **1** and **2**.

The ^{199}Hg NMR is a useful tool for the determination of the metal environment because the chemical shift is very sensitive to its coordination sphere. According to the literature, a decrease in the coordination number tends to give greater deshielding.[43–47] The spectra of **4**, **5**, **6** and **9** (Figure 6) showed signals at –1133.8, –1111.2, –1042.3 and –1124.1 ppm, respectively. The similarity of these shifts suggests that mercury had the same coordination number in all of the complexes and they are close to those found in other

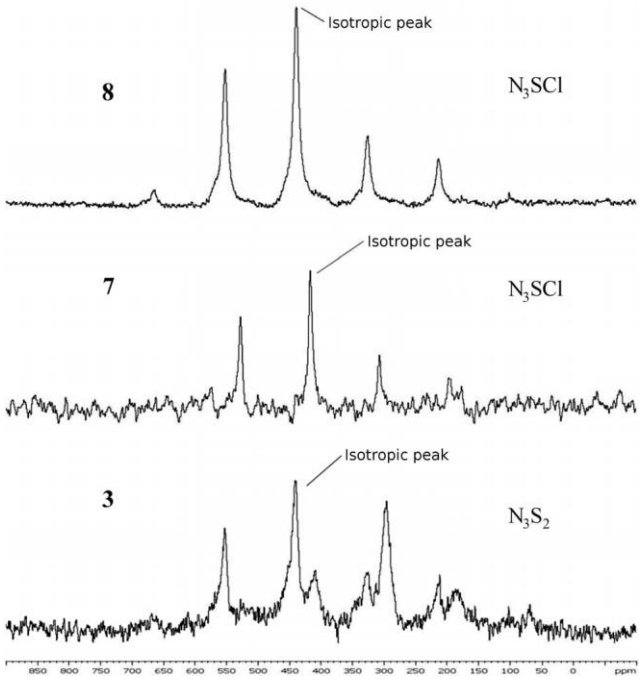


Figure 5. ^{113}Cd CP/MAS NMR spectra of **3**, **7** and **8**.

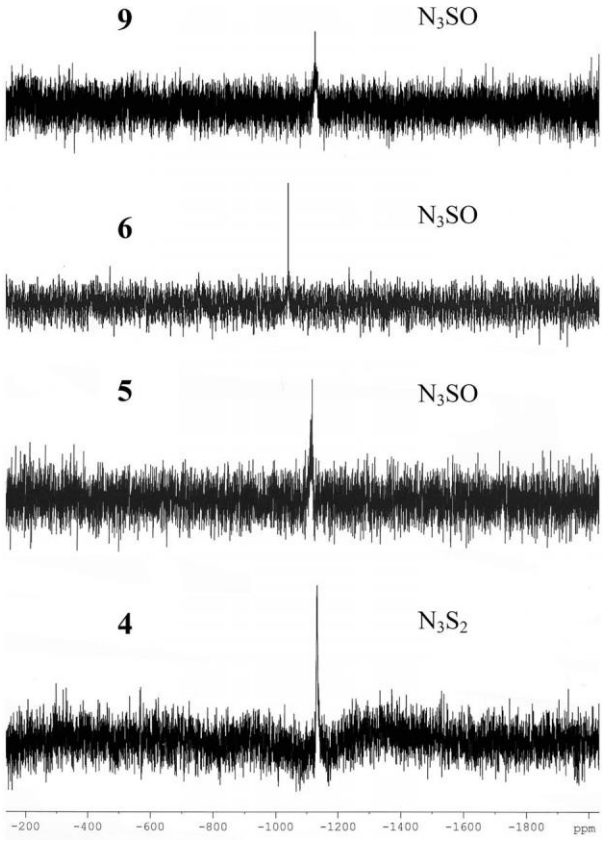


Figure 6. ^{199}Hg NMR spectra of **4**, **5**, **6** ([D$_6$]DMSO) and **9** (DMF + [D$_6$]DMSO) ppm.

thiosemicarbazonate complexes in which the metal is pentacoordinate.[44,48]

From the spectroscopic and analytical data, as well as the X-ray diffraction of **1**, **2** and **4**, we propose the structures summarized in Schemes 1 and 2 for the rest of the complexes.

Fluorescence

The fluorescence emission spectra of H_2AMeTsQ and its chloride salt [H_3AMeTsQ]Cl are shown in Figure 7. Both forms of the ligand show fluorescence emission at similar wavelengths, although for the neutral form it is more intense. This difference can be justified by a quenching of the fluorescence caused by the chloride ion. In fact, the decrease in the fluorescence intensity when the quinolinium chloride is formed makes quinoline species suitable as fluorescent sensors for the measurement of intracellular chloride ion levels.[49]

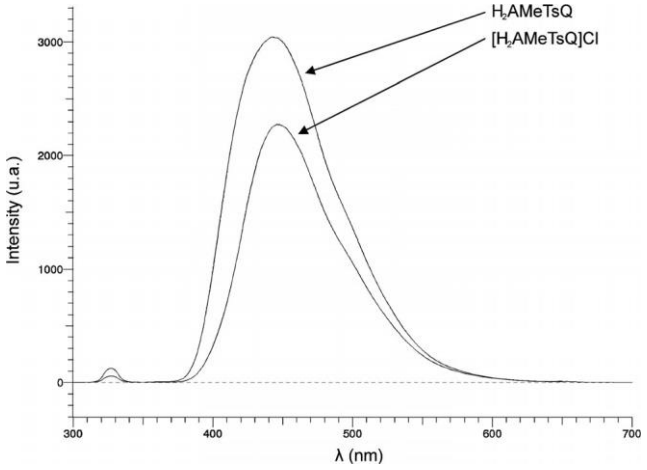


Figure 7. Emission spectra of H_2AMeTsQ and [H_3AMeTsQ]Cl (10^{-4} M) in DMSO (λ_{exc} = 325 nm).

Excitation of the complexes revealed a general quenching of the fluorescence intensity. One maximum was observed for **1**, **4**, **7** and **9**, two were observed for **3** and **8**, which were considerably shifted with respect to that of H_2AMeTsQ (Figure 8), and complexes **2**, **5** and **6** were not fluorescent; in general, the cadmium derivatives were more fluorescent than the mercury complexes. For the cadmium compounds with a neutral ligand (**1** and **7**), the highest fluorescence intensity was observed, followed by the mercury complex **9**, which also contains a neutral ligand. In **1** and **7**, the maximum was not significantly shifted with respect to that of the uncoordinated ligand, whereas in **9** it was shifted to higher wavenumbers by 10 nm. The other complexes showed significantly lower intensities. From these data, it can be clearly concluded that deprotonation of the ligand induces a decrease or a loss of the fluorescence emission and reveals the importance of the electronic delocalization in the quinoline ring, even when deprotonation takes place in the thiosemicarbazone arm. The fluorescence quenching might take place through a photoluminiscent electron transfer mechanism, in which electron delocalization on the quinoline ring increases upon complexation and decreases the fluorescence emission.[50,51] This charge delocalization increases when the ligand is deprotonated, so the fluorescence intensity of the complexes with the neutral ligand is, in general, higher.

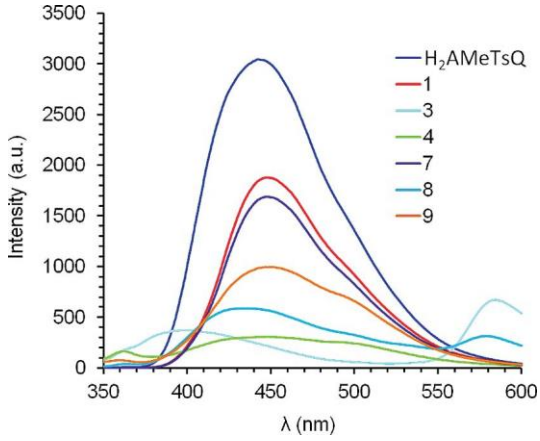


Figure 8. Emission spectra of H_2AMeTsQ, **1**, **4**, **7**, **8** and **9** (10^{-4} M) in DMSO (λ_{exc} = 325 nm).

Conclusions

A new dissymmetric thiosemicarbazone ligand containing a hydrazonequinoline limb, H_2AMeTsQ, was synthesized as well as its chloride salt [H_3AMeTsQ]Cl, and the reactivity of both ligands with cadmium and mercury nitrate was explored. Owing to the different acidity of the NH hydrogen atoms, the charge of the ligand could be controlled by the use of stoichiometric amounts of lithium hydroxide, which led to the formation of complexes with different structural characteristics. In all of the complexes, the ligand binds in a tetradentate N_3S mode and in some complexes also as a bridge through the sulfur atom to form dimeric species and a coordination polymer. Both forms of the ligand showed fluorescence emission, although the neutral ligand was more fluorescent than the salt. Complexation induced a quenching of the fluorescence emission, especially when the ligand was singly or doubly deprotonated.

Experimental Section

Materials and General Methods: All reagents were obtained from standard commercial sources and were used as received.

Caution! *Mercury and cadmium are highly toxic cumulative poisons, and their compounds should be handled carefully.*

Microanalyses were performed with a LECO CHNS-932 Elemental Analyzer. IR spectra in the 4000–400 cm^{-1} range were recorded as KBr pellets with a Jasco FT/IR-410 spectrophotometer. Fast atom bombardment mass spectra were recorded with a VG Auto Spec instrument using Cs as the fast atom and *m*-nitrobenzylalcohol (*m*-NBA) as the matrix. Electrospray mass spectrometry experiments were performed with an ion trap instrument LCQ Deca XP plus (Thermo Instruments). An ESI source was used in positive ioniza-

tion mode. Conductivity was measured using a freshly prepared DMF solution (ca. 10^{-3} m) at 25 °C with a Crison EC-Meter BASIC 30+ instrument. ^{1}H, ^{13}C, ^{113}Cd and ^{199}Hg NMR spectra were recorded with a Bruker AMX-300 spectrometer using [D6]DMSO or DMF/[D6]DMSO as solvents and using tetramethylsilane (TMS, ^{1}H and ^{13}C), $CdMe_2$ and $HgMe_2$ as internal references. ^{113}Cd and ^{199}Hg NMR experiments were recorded at 298 K using 10^{-1} m solutions. ^{13}C CP/MAS NMR spectra were recorded at 298 K with a Bruker AV400WB spectrometer equipped with a 4 mm MAS NMR probe and were obtained using a cross-polarization pulse sequence. The external magnetic field was 9.4 T, the sample was spun at 10–14 kHz and the spectrometer frequency was 100.61 MHz. For the recorded spectra, a contact time of 4 ms and recycle delays of 4 s were used. Chemical shifts are reported relative to TMS, using the CH group of adamantane as a secondary reference (δ = 29.5 ppm). ^{113}Cd CP/MAS NMR spectra were recorded with the same spectrometer, and the chemical shifts are reported relative to 0.1 m $Cd(ClO_4)_2$ and with $Cd(NO_3)_2{\cdot}4H_2O$ as secondary reference (–100 ppm). Fluorescence emission spectra were recorded with a Hitachi F-4500 fluorescence spectrophotometer using freshly prepared DMSO solutions (ca. 10^{-4} m) at 25 °C.

2-Hydrazinoquinoline: A suspension of 2-chloroquinoline (1.50 g, 9.17 mmol) in hydrazine monohydrate (3 mL, 61.85 mmol) was stirred under reflux for 2 h. The orange solid formed was collected by filtration, washed with 100 mL of water and dried in vacuo; yield 82% (1.20 g). $C_9H_9N_3$ (159.19): calcd. C 67.90, H 5.70, N 26.40; found C 67.50, H 5.64, N 26.30. ^{1}H NMR (300 MHz, [D6]-DMSO): δ = 8.04 (s, 1 H, NH), 7.86 (d, ^{3}J = 9.0 Hz, 1 H, 6-H), 7.60 (dd, ^{4}J = 1.1, ^{3}J = 7.9 Hz, 1 H, 9-H), 7.56–7.44 (m, 2 H, 11-H, 12-H), 7.15 (ddd, ^{4}J = 1.4, ^{3}J = 6.8, ^{3}J = 8.0 Hz, 1 H, 10-H), 6.84 (d, ^{3}J = 9.0 Hz, 1 H, 5-H), 4.30 (s, 2 H, NH_2) ppm. ^{13}C NMR (300 MHz, [D6]DMSO): δ = 159.6 (C-4), 147.9 (C-6), 136.8 (C-8), 129.6 (C-11), 128.0 (C-9), 125.9 (C-12), 123.8 (C-10), 121.9 (C-7), 111.7 (C-5) ppm. MS (EI+): m/z = 159.1 (100) $[M^{\cdot}]^{+}$.

Diacetyl-2-(4-methyl-3-thiosemicarbazone): This compound was synthesized from 2,3-butanedione (diacetyl) and 4-methyl-3-thiosemicarbazide, in water and in the presence of conc. HCl at 0 °C, in accordance with a previously reported procedure.[52] ^{1}H NMR (300 MHz, [D6]DMSO): δ = 10.65 (s, 1 H, NH), 8.62 (m, 1 H, N*H*CH_3), 3.05 (d, 3 H, NHC*H*$_3$), 2.42 (s, 3 H, CH_3C=O), 1.96 (s, 3 H, CH_3C=N) ppm. ^{13}C NMR (300 MHz, [D6]DMSO): δ = 197.45 (C=O), 178.90 (C=S), 145.45 (C=N), 31.37 ($NHCH_3$), 24.73 (CH_3C=O), 9.99 (CH_3C=N) ppm. MS (ESI+): m/z = 174.1 $[M + H]^{+}$.

H_2AMeTsQ: To a suspension of HAMeTs (0.50 g, 2.89 mmol) in dry methanol (15 mL), a solution of 2-hydrazinoquinoline (0.46 g, 2.89 mmol) in dry methanol (17 mL) was added. The mixture was stirred at room temperature for 24 h. The pale-yellow solid formed was collected by filtration, washed with methanol and dried in vacuo; yield 68% (0.62 g). $C_{15}H_{18}N_6S$ (314.41): calcd. C 57.30, H 5.77, N 26.73, S 10.20; found C 57.20, H 5.60, N 26.65, S 10.10. IR (KBr): $\tilde{\nu}$ = 3343 (s), 3309 (s), 3229 [s, ν(NH)]; 1619 (m), 1606 (s), 1575 (m), 1551 [s, ν(C=N) and thioamide II], 866 (w, thioamide IV) cm^{-1}. ^{1}H NMR (300 MHz, [D6]DMSO): δ = 10.33 (s, 1 H, 3-H), 10.14 (s, 1 H, 2-H), 8.31 (q, ^{3}J = 4.6 Hz, 1 H, 1-H), 8.20 (d, ^{3}J = 8.8 Hz, 1 H, 6-H), 7.80 (d, ^{3}J = 7.9 Hz, 1 H, 9-H), 7.70–7.55 (m, 3 H, 5-H, 11-H, 12-H), 7.31 (t, ^{3}J = 7.3 Hz, 1 H, 10-H), 3.04 (d, ^{3}J = 4.6 Hz, 3 H, 15-H), 2.26 (s, 6 H, 13-H, 14-H) ppm. ^{13}C NMR (300 MHz, [D6]DMSO): δ = 178.9 (C-1), 156.4 (C-4), 149.1, 147.4 (C-2, C-3), 145.5 (C-8), 138.6 (C-6), 130.3 (C-11), 128.4 (C-9), 126.3 (C-12), 125.0 (C-10), 123.5 (C-7), 110.3 (C-5), 31.7 (C-15), 12.0, 11.5 (C-13, C-14) ppm. MS (ESI+): m/z = 315.1 $[M + H]^{+}$.

[H_3AMeTsQ]Cl: This compound was prepared following the same procedure described above, but in the presence of conc. HCl (0.35 mL, 3.96 mmol). The suspension was stirred at room temperature for 24 h. The yellow precipitate formed was collected by filtration, washed with methanol and dried in vacuo; yield 91 % (0.92 g). If less hydrochloric acid than the stoichiometric amount was added, a mixture of H_2AMeTsQ and [H_3AMeTsQ]Cl was obtained. Both compounds can be easily isolated due to their different solubilities; [H_3AMeTsQ]Cl is less soluble. $C_{15}H_{19}ClN_6S$ (350.87): calcd. C 51.35, H 5.46, N 23.95, S 9.14; found C 51.41, H 5.48, N 24.09, S 9.10. IR (KBr): $\tilde{\nu}$ = 3377 (w), 3302 (m), 3279 (s), 3225 [s, ν(NH)], 1652 (vs), 1614 (m), 1606 (s), 1546 [s, ν(C=N) and thioamide II], 822 (w, thioamide IV) cm^{-1}. ^{1}H NMR (300 MHz, [D6]-DMSO): δ = 13.03 (br. s, 0.3 H, 6a-H), 12.28 (br. s, 0.8 H, 3-H), 10.41 (s, 1 H, 2-H), 8.55 (d, ^{3}J = 9.4 Hz, 1 H, 6-H), 8.51 (q, ^{3}J = 4.4 Hz, 1 H, 1-H), 8.11 (br. s, 1 H, 5-H), 8.01 (d, ^{3}J = 7.7 Hz, 1 H, 9-H), 7.85 (t, ^{3}J = 7.4 Hz, 1 H, 11-H), 7.77 (d, ^{3}J = 9.4 Hz, 1 H, 12-H), 7.57 (t, ^{3}J = 7.5 Hz, 1 H, 10-H), 3.05 (d, ^{3}J = 4.5 Hz, 3 H, 15-H), 2.45 (s, 3 H, 13-H or 14-H), 2.39 (s, 3 H, 13-H or 14-H) ppm. ^{13}C CP/MAS NMR (400 MHz): δ = 178.2 (C-1), 152.8 (C-4, C-2, C-3), 143.0 (C-8), 136.0 (C-6), 133.9 (C-11), 132.0 (C-9), 126.8 (C-12), 122.8 (C-10), 117.3 (C-7), 109.7 (C-5), 33.0 (C-15), 12.9 (C-13, C-14) ppm. MS (ESI+): m/z = 315.1 $[M]^{+}$.

[$Cd(NO_3)(H_2AMeTsQ)(H_2O)]NO_3{\cdot}2H_2O$ (1): To a suspension of H_2AMeTsQ (100 mg, 0.32 mmol) in methanol (30 mL), a solution of cadmium nitrate tetrahydrate (100 mg, 0.32 mmol) in methanol (2 mL) was added. The solution was stirred under reflux for 8 h. The yellow precipitate formed was collected by filtration, washed with methanol and dried in vacuo; yield 75 % (0.145 g). Yellow crystals suitable for X-ray diffraction were obtained by slow evaporation of the mother liquor. M.p. 247 °C (decomposition). Λ_M = 69.5 $\Omega^{-1}\,cm^2\,mol^{-1}$. $C_{15}H_{24}CdN_8O_9S$ (604.86): calcd. C 29.78, H 4.00, N 18.53, S 5.30; found C 30.02, H 3.88, N 18.62, S 5.36. IR (KBr): $\tilde{\nu}$ = 3433 (m), 3234 (m), 3125 (w), 3225 [s, ν(OH), ν(NH)], 1646 (s), 1621 (m), 1577 (s), 1505 [m, ν(C=N), thioamide II, + δ(H_2O)], 1384 [s, ν(NO)], 839 (w, thioamide IV) ppm. ^{13}C NMR (300 MHz, [D6]DMSO): δ = 179.1 (C-1), 157.1 (C-4), 150.7, 147.4 (C-2, C-3), 144.1 (C-8), 137.0 (C-6), 133.2 (C-11), 129.3 (C-9), 126.4 (C-12), 123.3 (C-10), 119.7 (C-7), 112.9 (C-5), 31.8 (C-15), 13.2, 12.4 (C-13, C-14) ppm. ^{13}C CP/MAS NMR (400 MHz): δ = 173.6 (C-1), 155.0 (C-4), 151.6, 148.6 (C-2, C-3), 143.1 (C-8), 136.1 (C-6), 132.2 (C-11), 128.6 (C-9), 125.4 (C-12), 122.4 (C-10, C-7), 112.7 (C-5), 32.8 (C-15), 12.5, 10.4 (C-13, C-14) ppm. ^{113}Cd NMR (300 MHz, [D6]DMSO): δ = 122.2 ppm. MS (ESI+): m/z = 427.0 $[Cd(HAMeTsQ)]^{+}$. This complex can also be obtained from [H_3AMeTsQ]Cl.

[$Cd(HAMeTsQ)(CH_3OH)]_2(NO_3)_2{\cdot}2H_2O$ (2): A solution of cadmium nitrate tetrahydrate (69 mg, 0.22 mmol) in methanol (2 mL) was added to a suspension of H_2AMeTsQ (70 mg, 0.22 mmol) and $LiOH{\cdot}H_2O$ (9 mg, 0.22 mmol) in methanol (20 mL). The suspension was stirred under reflux for 5 h. The scarce amount of solid formed was separated by filtration and discarded, and then the solvent was partially evaporated and cooled to 4 °C until a yellow solid precipitated, which was collected by filtration, washed with cold methanol and dried in vacuo; yield 71 % (0.084 g). Yellow crystals suitable for X-ray analysis were obtained by slow evaporation of mother liquor. M.p. 262 °C (decomposition). Λ_M = 185.5 $\Omega^{-1}\,cm^2\,mol^{-1}$. $C_{32}H_{46}Cd_2N_{14}O_{10}S_2$ (1075.72): calcd. C 35.73, H 4.31, N 18.23, S 5.96; found C 35.69, H 4.23, N 18.14, S 5.85. IR (KBr): 3433 (m), 3276 (s), 3229 [s, ν(OH), ν(NH)], 1638 (w), 1615 (s), 1608 (s), 1588 (w), 1540 [s, ν(C=N), thioamide II, δ(H_2O)], 1385 [s, ν(NO)], 831(w, thioamide IV) cm^{-1}. ^{13}C NMR (300 MHz, [D6]DMSO): δ = 175.0 (C-1), 152.5 (C-4), 145.8 (C-2, C-3), 143.7

(C-8), 140.6 (C-6), 131.8 (C-11), 129.0 (C-9), 125.8 (C-12), 125.1 (C-10), 125.0 (C-7), 113.3 (C-5), 30.0 (C-15), 15.0, 14.8 (C-13, C-14) ppm. ^{113}Cd NMR (300 MHz, [D$_6$]DMSO): δ = 249.7 ppm. MS (FAB+): *m*/*z* (%) = 851.0 (7) [Cd$_2$(HAMeTsQ)$_2$ + H]$^+$, 427.0 (70) [Cd(HAMeTsQ)]$^+$.

[Cd(AMeTsQ)]$_2$·H$_2$O (3): A solution of cadmium nitrate tetrahydrate (71 mg, 0.23 mmol) in methanol (2 mL) was added to a suspension of H$_2$AMeTsQ (70 mg, 0.22 mmol) and LiOH·H$_2$O (19 mg, 0.44 mmol) in the same solvent (20 mL). The suspension was stirred for 24 h at room temperature. The red precipitated formed was collected by filtration, washed with methanol and dried in vacuo; yield 87 % (0.085 g). M.p. 150 °C (decomposition). Λ_M = 2.7 Ω^{-1} cm^2 mol^{-1}. $C_{30}H_{34}Cd_2N_{12}OS_2$ (867.60): calcd. C 40.68, H 4.10, N 18.98, S 7.24; found C 40.94, H 4.16, N 19.15, S 7.36. IR (KBr): $\tilde{\nu}$ = 3430 (s), 3322 (s), 3203 [m, ν(OH), ν(NH)], 1617 (s), 1546 (s), 1529 [s, ν(C=N), thioamide II, δ(H$_2$O)], 822 (w, thioamide IV) cm^{-1}. ^{13}C NMR (300 MHz, [D$_6$]DMSO): δ = 173.8 (C-1), 161.5 (C-4), 147.5, 146.4 (C-2, C-3), 142.5 (C-8), 136.3 (C-6), 130.0 (C-11), 128.0 (C-9), 124.2 (C-12), 123.2 (C-10), 121.3 (C-7), 121.0 (C-5), 29.9 (C-15), 14.8, 13.8 (C-13, C-14) ppm. ^{113}Cd NMR (300 MHz, [D$_6$]DMSO): δ = 307.2 ppm. ^{113}Cd CP/MAS NMR (400 MHz): δ = 441.4 ppm. MS (ESI+): *m*/*z* = 427.0 [Cd(HAMeTsQ)]$^+$. This complex can also be synthesized from [H$_3$AMeTsQ]Cl in the presence of three mol of lithium hydroxide.

[[Hg(HAMeTsQ)]NO$_3$·H$_2$O]$_n$ (4): To a suspension of H$_2$AMeTsQ (75 mg, 0.24 mmol) in methanol (20 mL), a suspension of mercury nitrate monohydrate (82 mg, 0.24 mmol) in methanol (2 mL) was added. The mixture was stirred at room temperature for 3 d. The yellow solid formed was collected by filtration, washed with methanol and dried in vacuo; yield 78 % (0.111 g). Suitable crystals for X-ray diffraction were obtained by slow evaporation of a solution in DMSO. M.p. 135 °C (decomposition). Λ_M = 78.4 Ω^{-1} cm^2 mol^{-1}. $C_{15}H_{19}HgN_7O_4S$ (594.01): calcd. C 30.32, H 3.23, N 16.51, S 5.39; found C 30.05, H 3.38, N 16.70, S 5.47. IR (KBr): $\tilde{\nu}$ = 3334 (m), 3222 (m), 3191 (m), 3146 [m, ν(OH) + ν(NH)], 1648 (m), 1617 (s), 1606 (s), 1540 [m, ν(C=N), thioamide II, δ(H$_2$O)], 1385 [s, ν(NO)], 835 (w, thioamide IV) cm^{-1}. ^{13}C NMR (300 MHz, [D$_6$]DMSO): δ = 167.7 (C-1), 151.8 (C-4), 146.2, 144.8 (C-2, C-3), 142.6 (C-8), 141.9 (C-6), 132.6 (C-11), 129.4 (C-9), 125.8 (C-12), 125.4 (C-10), 125.0 (C-7), 114.1 (C-5), 29.9 (C-15), 14.0, 13.0 (C-13, C-14) ppm. ^{199}Hg NMR (300 MHz, [D$_6$]DMSO): δ = 1133.8 ppm. MS (ESI+): *m*/*z* = 515.1 [Hg(HAMeTsQ)]$^+$.

[Hg(NO$_3$)(HAMeTsQ)] (5): A suspension of mercury nitrate monohydrate (76 mg, 0.22 mmol) in methanol (2 mL) was added to a suspension of H$_2$AMeTsQ (70 mg, 0.22 mmol) and LiOH·H$_2$O (9 mg, 0.22 mmol) in methanol (20 mL). The suspension was stirred at room temperature for 48 h. The orange solid was collected by filtration, washed with methanol and dried in vacuo; yield 77 % (0.098 g). M.p. 174 °C (decomposition). Λ_M = 47.0 Ω^{-1} cm^2 mol^{-1}. $C_{15}H_{17}HgN_7O_3S$ (575.99): calcd. C 31.27, H 2.98, N 17.03, S 5.55; found C 31.40, H 3.12, N 17.19, S 5.54. IR (KBr): $\tilde{\nu}$ = 3352 [m, ν(NH)], 1616 (m), 1544 (m), 1536 [m, ν(C=N), thioamide II], 1385 [s, ν(NO)], 827 (w, thioamide IV) cm^{-1}. ^{13}C NMR (300 MHz, [D$_6$]DMSO): δ = 168.1 (C-1), 151.9 (C-4), 146.2 (C-2, C-3), 142.9 (C-8), 141.6 (C-6), 132.4 (C-11), 129.3 (C-9), 125.6 (C-12), 125.4 (C-10), 125.0 (C-7), 114.1 (C-5), 29.7 (C-15), 15.1, 14.9 (C-13, C-14) ppm. ^{199}Hg NMR (300 MHz, [D$_6$]DMSO): δ = –1111.2 ppm. MS (ESI+): *m*/*z* = 515.1 [Hg(HAMeTsQ)]$^+$.

[Hg(AMeTsQ)(H$_2$O)] (6): To a suspension of H$_2$AMeTsQ (71 mg, 0.23 mmol) and LiOH·H$_2$O (20 mg, 0.48 mmol) in methanol (20 mL), a suspension of mercury nitrate monohydrate (79 mg, 0.23 mmol) in methanol (2 mL) was added. The mixture was stirred at room temperature for 24 h. The red solid formed was collected by filtration, washed with methanol and dried in vacuo; yield 95 % (0.116 g). M.p. 180 °C (decomposition). Λ_M = 2.8 Ω^{-1} cm^2 mol^{-1}. $C_{15}H_{18}HgN_6OS$ (531.00): calcd. C 33.92, H 3.42, N 15.83, S 6.02; found C 34.01, H 3.50, N 15.73, S 5.98. IR (KBr): $\tilde{\nu}$ = 3428 (m), 3332 [s, ν(OH), ν(NH)], 1617 (s), 1548 (s), 1532 [s, ν(C=N), thioamide II, δ(H$_2$O)], 811 (w, thioamide IV) cm^{-1}. ^{13}C NMR (300 MHz, [D$_6$]DMSO): δ = 160.9 (C-1), 148.8 (C-4), 145.5 (C-2, C-3), 144.8 (C-8), 135.9 (C-6), 130.2 (C-11), 128.2 (C-9), 124.2 (C-12), 123.4 (C-10), 121.9 (C-7), 121.4 (C-5), 29.8 (C-15), 14.9, 14.1 (C-13, C-14) ppm. ^{199}Hg NMR (300 MHz, [D$_6$]DMSO): δ = –1042.3 ppm. MS (ESI+): *m*/*z* = 515.1 [Hg(HAMeTsQ)]$^+$. This complex is also formed with [H$_3$AMeTsQ]Cl in the presence of two or three mol of lithium hydroxide.

Complexes from [H$_3$AMeTsQ]Cl: The reactions were carried out in the same conditions described for the complexes obtained from H$_2$AMeTs: metal to ligand ratio 1:1, in methanol as solvent and also in the absence or in the presence of 1, 2 or 3 equiv. of LiOH·H$_2$O.

[Cd(Cl)(H$_2$AMeTsQ)]NO$_3$·H$_2$O (7): This yellow compound was obtained in the presence of 1 mol of LiOH·H$_2$O; yield 79 % (0.056 g). M.p. 258 °C (decomposition). Λ_M = 69.3 Ω^{-1} cm^2 mol^{-1}. $CdC_{15}H_{20}N_7SO_4$ (506.84): calcd. C 35.55, H 3.98, N 19.34, S 6.33; found C 40.94, H 4.16, N 19.15, S 7.36. IR (KBr): $\tilde{\nu}$ = 3447 (m), 3188 (m), 3157 [m, ν(OH), ν(NH)], 1647 (m), 1615 (s), 1604 (s), 1583 (s), 1528 [s, ν(C=N), thioamide II, δ(H$_2$O)], 1385 [s, ν(NO)], 835 (w, thioamide IV) cm^{-1}. ^{13}C NMR (300 MHz, [D$_6$]DMSO): δ = 178.6 (C-1), 155.1 (C-4), 149.7, 147.9 (C-2, C-3), 143.5 (C-8), 139.6 (C-6), 130.9 (C-11), 128.6 (C-9), 124.6 (C-12), 124.1 (C-10), 113.2 (C-7), 111.1 (C-5), 31.7 (C-15), 12.2, 11.9 (C-13, C-14) ppm. ^{113}Cd CP/MAS NMR (400 MHz): δ = 418.1 ppm. MS (ESI+): *m*/*z* = 427.0 [Cd(HAMeTsQ)]$^+$.

[Cd(Cl)(HAMeTsQ)] (8): This complex was formed in the presence of 2 mol of LiOH·H$_2$O; yield 88 % (0.063 g). M.p. 288 °C (decomposition). Λ_M = 6.5 Ω^{-1} cm^2 mol^{-1}. $CdC_{15}H_{17}N_6SCl$ (461.27): calcd. C 39.06, H 3.71, N 18.22, S 6.95; found C 38.74, H 3.62, N 18.10, S 6.93. IR (KBr): $\tilde{\nu}$ = 3320 (s), 3195 (m), 3153 [w, ν(NH)], 1617 (s), 1608 (s), 1581 (m), 1531 [s, ν(C=N), thioamide II], 828 (w, thioamide IV). ^{13}C CP/MAS NMR (400 MHz): δ = 172.5 (C-1), 153.5 (C-4), 147.2 (C-2, C-3), 144.4 (C-8), 140.6 (C-6), 131.4 (C-11), 129.0 (C-9), 125.9 (C-12, C-10, C-7), 111.7 (C-5), 28.8 (C-15), 16.5 (C-13, C-14) ppm. ^{113}Cd CP/MAS NMR (400 MHz): δ = 439.7 ppm. MS (ESI+): *m*/*z* = 427.0 [Cd(HAMeTsQ)]$^+$.

[Hg(NO$_3$)(H$_2$AMeTsQ)]NO$_3$ (9): This complex was obtained in the absence or in the presence of 1 mol of LiOH·H$_2$O; yield 73 % (0.065 g). M.p. 202 °C (decomposition). Λ_M = 67.0 Ω^{-1} cm^2 mol^{-1}. $HgC_{15}H_{18}N_8SO_6$ (639.01): calcd. C 28.19, H 2.84, N 17.54, S 5.02; found C 28.24, H 2.99, N 17.60, S 5.84. IR (KBr): $\tilde{\nu}$ = 3353 (s), 3295 (s), 3194 (m), 3104 [w, ν(NH)], 1650 (s), 1617 (m), 1532 [w, ν(C=N), thioamide II], 1385 [s, ν(NO)], 828 (w, thioamide IV) cm^{-1}. ^{13}C CP/MAS NMR (400 MHz): δ = 170.4 (C-1), 152.4 (C- 4), 148.7, 145.3 (C-2, C-3), 141.1 (C-8, C-6), 135.0 (C-11), 129.7 (C-9), 126.6 (C-12), 122.2 (C-10), 119.8 (C-7), 112.6 (C-5), 29.2 (C-15), 17.5, 15.5 (C-13, C-14) ppm. ^{199}Hg NMR (300 MHz, [D$_6$]DMSO): δ = –1124.1 ppm. MS (ESI+): *m*/*z* = 515.0 [Hg(HAMeTsQ)]$^+$.

X-ray Crystallography: The data for **1**, **2** and **4** were acquired with a Bruker AXS Kappa Apex-II diffractometer equipped with an Apex-II CCD area detector with a graphite monochromator (Mo-K_α radiation, λ = 0.71073 Å). The substantial redundancy in data allowed empirical absorption corrections (SADABS)[53] to be applied by using multiple measurements of symmetry-equivalent re-

flections. The raw intensity data frames were integrated with the SAINT program, which also applied corrections for Lorentz and polarization effects.[54] The software package SHELXTL version 6.10 was used for space group determination, structure solution and refinement. The structures were solved by direct methods (SHELXS-97),[55] completed with difference Fourier syntheses and refined with full-matrix least-squares using SHELXL-97 to minimize $\omega(F_o^2 - F_c^2)$. Weighted R factors (R_w) and all goodness of fit (S) are based on F^2; conventional R factors (R) are based on F.[56] All non-hydrogen atoms were refined with anisotropic displacement parameters. The NH and OH hydrogen atoms were located in difference Fourier maps and their coordinates and isotropic thermal parameters were subsequently refined, except for H3 in **4**, which was positioned geometrically. CH hydrogen atoms were positioned geometrically after each cycle of refinement. For **4**, the hydrogen atoms of the water molecules could not be located in the difference Fourier map, presumably as a result of disorder. They have been omitted from the model but included in calculations of the formula weight etc. All scattering factors and anomalous dispersions factors are contained in the SHELXTL 6.10 program library.

CCDC numbers 883498 (for **1**), -883499 (for **4**) and -883500 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.cdcc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Table with the full bond lengths and angles as well as the hydrogen bonding information.

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