

Synthesis, Structural and Spectroscopic Studies of Novel Azo-Containing *N,O*-bonded Complexes in the α -Iminoketone and Azophenolate forms

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Este artigo descreve a síntese e a caracterização espectroscópica e estrutural por difratometria de raios X em monocristal de dois novos complexos contendo o grupamento azo, *cis*-bis[4-nitro-2-(4-nitrofenilazo)-fenolato- κN^1]bis(piridino- κN)cádmio(II), **1**, e *cis*-bis[2-(4-fenilazo-fenilimino)-2*H*-acenafteno-1-ona]dicloromercúrio(II), **2**. Embora os ligantes e os metais sejam diferentes, observa-se para os dois complexos uma coordenação do tipo *N,O*-bidentada ao átomo central. Em **1**, a coordenação é feita por um átomo de N do grupo azo e por um átomo de O do grupo fenolato, enquanto em **2** a coordenação ocorre exclusivamente via átomos de O e N da α -iminocetona. Ambos os complexos exibem interações intramoleculares do tipo π - π , que exercem um importante papel na determinação de suas estruturas moleculares, além de também exibirem arranjos supramoleculares governados por ligações de hidrogênio não-clássicas. Em adição, a estrutura de **2** é a primeira relatada na literatura com um novo tipo de ligante, a azo-iminocetona, e também a primeira contendo mercúrio complexado a uma α -iminocetona.

This article describes the synthesis and the spectroscopic and structural characterization of two novel azo-containing complexes, *cis*-bis[4-nitro-2-(4-nitrophenylazo)-phenolate- κN^1]bis(piridino- κN)cadmium(II), **1**, and *cis*-bis[2-(4-phenylazo-phenylimino)-2*H*-acenaphthylene-1-one]dichloromercury(II), **2**. In spite of the different metal centres, both complexes show an *N,O*-bidentate complexation to the metal. In **1** the metal coordinates to an azo N and to a phenolate O atom, whereas in **2** the metal binds to an O and an N atom of the α -iminoketone. Both complexes show intramolecular π - π interactions, which play an important role in their molecular structures. In addition they also present non-classical H-bonding, which is crucial to their supramolecular arrangements. Moreover, **2** is the first case in the literature of a complex with a new class of ligand, an azoiminoketone, as well as the first case of an α -iminoketone Hg complex.

Keywords: α -iminoketone, azo-group, π - π interactions, non-classical H-bonds

Introduction

The chemistry of polynitrogenated systems has been studied by several research groups because of their versatile application in various fields.¹ These substances show important chemical and physical properties, leading to new compounds with unique characteristics.²⁻⁴ Specific aromatic diazenes are the dominant class of synthetic organic colorants.⁵ These compounds are the most widely used class of dyes, as in textiles and fibres, as colorants in printing, and in high-technology areas, as in ink-jet printers.⁵ The reversible interconversion of the *cis* and *trans* isomers of azo compounds allows the use

of these substances in optical data storage and switching devices.⁵ Such optical properties depend not only on the spectroscopic behavior of the molecules but also on their crystallographic arrangement.⁵ α -Diimines, also a class of polynitrogenated ligands, are commonly used in catalysis for the polymerization of olefins, being constituents of the so-called Brookhart catalysts.⁶ Several research groups have replaced α -diimines for α -iminoketones in these catalysts with good results.⁷

Although several complexes have been reported with α -diimines,⁸ until the present only 11 structures containing α -iminoketones can be found in the Cambridge Structural Database for transition-metal complexes. The reason for this scarcity may lie in part on their weaker electron donor character compared to α -diimines.⁹ The present article presents the synthesis and the spectroscopic and

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crystallographic characterization of two azo-containing complexes, *cis*-bis[4-nitro-2-(4-nitrophenylazo)-phenolate- κN^1]bis(piridine- κN)cadmium(II), **1**, showing an azo-phenolate linkage to Cd, and *cis*-bis[2-(4-phenylazo-phenylimino)-2H-acenaphthylen-1-one] dichloromercury(II), **2**, with an N=C–C=O grouping in a bidentate complexation to Hg.

This study led to some unusual findings, namely the great importance of intramolecular π - π interactions in the determination of the conformations of the complexes, as well as of the non-classical intermolecular H-bonding, which played a significant role in the crystalline arrangement of the solids.

Experimental

The synthesis of **1**, Scheme 1, was started by mixing 10.0 mL of MeOH, 10.0 mL of Me₂CO and 5.0 mL of py with 0.0576 g (0.2 mmol) of commercial 4-nitro-2-(4-nitrophenylazo)-phenol (**L1**), which was added with continuous stirring at room temperature (r.t.). After 20 min, 0.0266 g (0.1 mmol) of cadmium(II) acetate was added. Stirring was maintained for 24 h. The solution was filtered off and red prism-shaped crystals suitable for X-ray analysis were obtained by slow evaporation of the mixture at r.t. with a yield of 76%.

Properties of **1**

Decomposed at $T > 250$ °C; compound **1** (Found C, 48.55; H, 2.67; N, 15.17. Calc. for C₃₄H₂₄CdN₁₀O₁₀: C, 48.33; H, 2.86; N, 16.58%); IR ν_{\max} /cm⁻¹: (**L1**, 4000-600 in CsI pellets) 1408 (N=N), 956 (C–N=N–C), 1526 (NO₂), 3428 (O–H); (**1**, 4000-200 cm⁻¹ in CsI pellets) 1597, 1559,

1518 (NO₂), 1501, 1447, 1402 (N=N), 1343, 1311, 1230, 1142, 1109, 1070, 1036, 1009, 973 (C–N=N–C), 921, 852, 830, 799, 753, 704, 679, 645, 627, 583, 571, 550, 514F, 494, 460, 418, 405, 376, 251, 230, 224, 202.

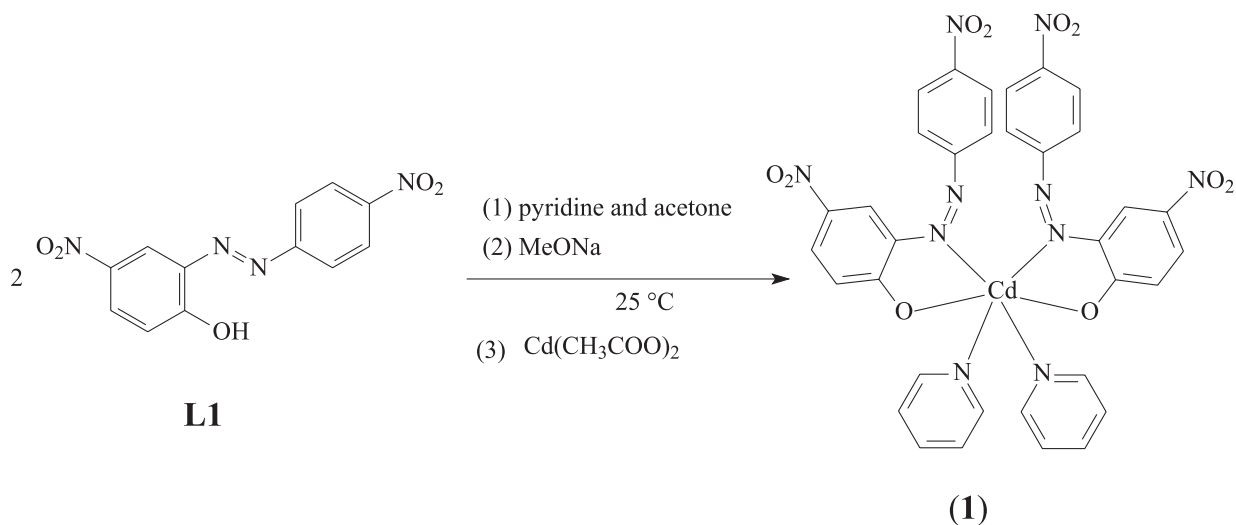
The synthesis of **2**, Scheme 2, was obtained by the “one-pot reaction” already used by us in the preparation of other α -diimine complexes.¹⁰ 0.5465 g (3.0 mmol) of commercial acenaphthenequinone was placed to react with 0.5917 g (3.0 mmol) of *p*-aminoazobenzene in 50 mL of MeOH in a 100 mL flask. The solution was heated under reflux for two hours and, after this time, 0.8145 g (3.0 mmol) of HgCl₂ was added. An intensely red precipitate was promptly formed. This was isolated by filtration and recrystallized from MeOH, with a 79% yield.

Properties of **2**

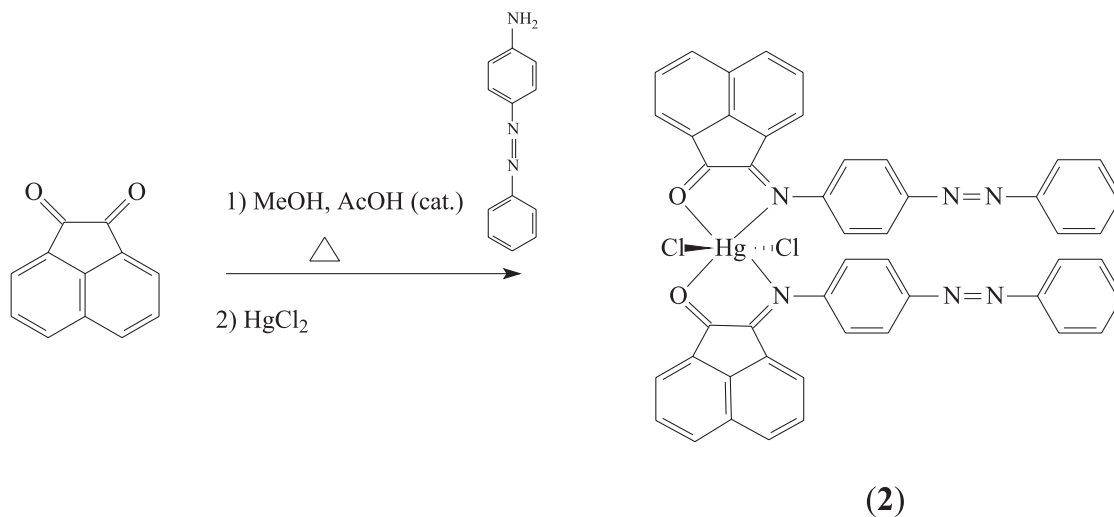
mp 180°C; IR ν_{\max} /cm⁻¹ (4000-600 cm⁻¹ in CsI pellets; 600-50 cm⁻¹ in polyethylene film): 3062, 3036, 3018, 1731, 1655, 1604, 1589, 1488, 1464, 1437, 1424, 1407, 1276, 1226, 1180, 1138, 1101, 1072, 1031, 1018, 1006, 911, 847, 779, 767, 739, 694, 687, 556, 241F, 490, 412, 377, 292, 280.

X-ray data

For **1** the X-ray data were collected at 295 K from an Enraf-Nonius Kappa-CCD¹¹ diffractometer with graphite monochromatized Mo K α radiation. The cell parameters were obtained using the COLLECT¹¹ and PHICHI¹² programs. The X-ray diffraction data for **2** were collected at 295 K from a Bruker APEXII-CCD¹³ diffractometer with graphite monochromatized Mo K α radiation. Cell parameters were obtained and refined using the SAINT¹³ program. Lorentz



Scheme 1.



Scheme 2.

polarization was corrected with the EvalCCD¹⁴ program for **1** and with the SAINT¹³ program for **2**. Absorption corrections were performed with the SADABS¹³ program. The two structures were solved by SHELXS-97 Direct Methods,¹⁵ and refined with SHELXL-97,¹⁶ contained within the WinGX-32 crystallographic program.¹⁷ For **1** and **2** the positional parameters of the H atoms bonded to C atoms in the phenyl and acenaphthene rings were obtained geometrically, with the C–H distances fixed at 0.93 Å for C_{sp^2} atoms, and set to ride on their respective C atoms, with $U_{iso}(H) = 1.2U_{eq}(C_{sp^2})$. In **2** there is an order and disorder effect for one of the azo groups (N5–N6), which does not take part either in the coordination or in the weak interactions. Because of this effect these atoms were refined isotropically. X-ray data are collated in Table 1.

Results and Discussion

IR data

Both complexes were analyzed by IR spectroscopy and all absorptions were registered using a Perkin Elmer Spectrum One IR spectrometer. The compounds presented bands characteristic of their functional groups, of which the more significant for both ligands and complexes are herein reported.

These bands show symmetrical and anti-symmetrical stretching and deformations of the groups (N=N), (O–H), (NO₂), (C=O), (C=N) and (C=C). Special attention was given to the absorptions of C=O, N=N and O–H bonds. **L1** binds to metals in its anionic form (R–O)[–]. The IR spectrum of the azo derivatives shows broad OH absorptions centered around 3400 cm^{–1} due to intramolecular hydrogen bonding between those groups and N atoms of the azo group.^{18–21}

This band is absent in **1**, indicating the replacement of the OH proton by the metal.

The unique band at 1500 to 1530 cm^{–1} is typical of the NO₂ absorptions. It does not show any appreciable shift in **1**, suggesting that the NO₂ group is not involved in complexation.

A medium absorption seen in all the ligands around 1695 cm^{–1} is due to the $\nu(C=N)$ stretch originating from the tautomerization of the C–N linkage.

A weak band at 1420–1450 cm^{–1} was assigned to the unsymmetrical stretching of the usually inactive $\nu(N=N)$ linkage; this is what is also seen in the cases of *trans-p*-substituted azobenzenes²¹ and arylazo naphthols.¹⁸ These bands undergo a shift to higher wavenumbers of 12–16 cm^{–1} upon complexation, suggesting the involvement of the azo nitrogen in chelation. The band at 973 cm^{–1} associated with $\nu(C-N=N-C)$ stretching is found at higher wavenumbers upon metal complexation. The unaffected frequencies at 1590–1620 cm^{–1} were assigned to the aromatic $\nu(C=C)$ vibrations.²¹

The success in the preparation of **2** is shown by two strong new bands in its IR spectrum, which appear at 1731 and 1655 cm^{–1}. These bands correspond to the $\nu(CO)$ and $\nu(C=N)$ absorptions of the α -iminoketone. The latter band can be used as a probe to follow the progress of the reaction. Another important band is that corresponding to the $\nu(N=N)$ stretching vibration of the azo group; this absorption falls around 1400 cm^{–1}.¹⁸ In the present case, the band occurs at 1407 cm^{–1}. The low frequency region also provides data for the elucidation of the molecular structure as well as on the environment of the coordination sphere.²² Three medium intensity bands were recorded here. The new band at 377 cm^{–1} can be assigned to $\nu(Hg-N)$, whereas that at 292 cm^{–1} relates to $\nu(Hg-O)$; the third absorption in this

Table 1. Crystal and experimental data for **1** and **2**

Empirical formula	C ₃₄ H ₂₄ N ₁₀ O ₁₀ Cd (1)	C ₄₈ H ₃₀ N ₆ O ₂ HgCl ₂ (2)
Formula weight	845.04	994.27
T / K	295(2)	295(2)
Radiation, λ / Å	0.71073	0.71073
Crystal system, Space group	Monoclinic, <i>P2₁/n</i>	Monoclinic, <i>P2₁/n</i>
Unit cell dimensions / Å and °	<i>a</i> = 16.356(3) <i>b</i> = 11.396(2) <i>c</i> = 20.192(4) β = 111.51(3)	<i>a</i> = 9.2575(2) <i>b</i> = 15.0721(3) <i>c</i> = 29.7675(7) β = 94.727(2)
Volume / Å ³	3501.6(12)	4139.33(16)
Z	4	4
Calculated density / g cm ⁻³	1.603	1.595
Absorption coefficient / mm ⁻¹	0.698	3.895
<i>F</i> (000)	1704	1960
Crystal size / mm	0.20 x 0.18 x 0.16	0.17 x 0.15 x 0.12
Theta range / °	2.68 to 25.00 °	2.59 to 24.70
Reflections collected	31414	35596
Independent reflections	6113 [<i>R</i> _(int) = 0.1030]	7022 [<i>R</i> _(int) = 0.0906]
Completeness to θ max.	99.0 %	99.9 %
Max. and min. transmission	0.8966 and 0.8731	0.6479 and 0.5489
Observed data / restraints / parameters	6113 / 0 / 496	7022 / 0 / 524
Goodness-of-fit on <i>F</i> ²	1.053	0.865
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0480 <i>wR</i> ₂ = 0.0863	<i>R</i> ₁ = 0.0416 <i>wR</i> ₂ = 0.0890
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1161 <i>wR</i> ₂ = 0.1015	<i>R</i> ₁ = 0.1075 <i>wR</i> ₂ = 0.1088
Largest diff. peak and hole / e ⁻ Å ⁻³	0.620 and -0.429	0.660 and -0.579

region is that at 280 cm⁻¹, which is typical of ν(Hg–Cl) vibrations.

Crystallographic results

ORTEP-3²³ representations of complexes **1** and **2** are shown in Figures 1a and 1b. Bond lengths and bond angles are listed in Table 2. The other figures were generated with the DIAMOND²⁴ program.

Complex **1** has non-classical intramolecular C–H...O hydrogen bonds and π–π interactions, which help to stabilize its structure in the conformation shown (Figure 1a). On the other hand, the crystal packing is dictated by intermolecular C–H...O hydrogen bonds (Figure 2). The charge in cadmium(II) is stabilized by two deprotonated 4-nitro-2-(4-nitrophenylazo)-phenolate ligands *via N,O* monometallic bidentate bonds, and the coordination sphere is completed by two pyridine co-ligands. The structure of **1** shows a pseudooctahedral environment with the pyridine ligands in a mutual *cis* arrangement, and the chelating **L1** ligands arranged with their O atoms mutually *trans* and their N atoms *cis*. The distortion of the geometry around the metal

is due to steric effects and intramolecular interactions. The two five-membered chelate rings are also responsible for an additional deviation, because the bite angle is reduced from the octahedral 90° angle. The bite angles as well as other important angles are presented in Table 2. The molecular structure of **1** shows the expected *trans* stereochemistry about the N1=N2 and N5=N6 double bonds. The bond lengths for **1** are also shown in Table 2. The accepted mean value for N=N is 1.24 Å, whereas for C_{aryl}–N it is 1.44 Å (International Tables for X-ray Crystallography, 2006, Vol. C).²⁵ In our structure, the increase in the N=N bond and the decrease in the C_{aryl}–N bond suggest a delocalization of the azo π-electrons towards the aryl groups. The N=N bond lengths in **1** are also comparable with those of bis(3-methyl-1-phenyl-4-(quinolin-8-yl-diazonyl)-5-thiolatopyrazole-*N,N',S*)cadmium(II), for which N=N is 1.285 Å.²⁶ The phenyl rings in **1** show small deviations from planarity, with root mean square (r.m.s.) values of 0.021 Å for C₁₁–C₁₆, 0.009 Å for C₂₁–C₂₆, 0.013 Å for C₃₁–C₃₆, and 0.011 Å for C₄₁–C₄₆. The dihedral angle between the C₁₁–C₁₆ and C₂₁–C₂₆ phenyl rings is 52.8(1)°, and between C₃₁–C₃₆ and C₄₁–C₄₆ is 53.1(1)°. The O1 atom

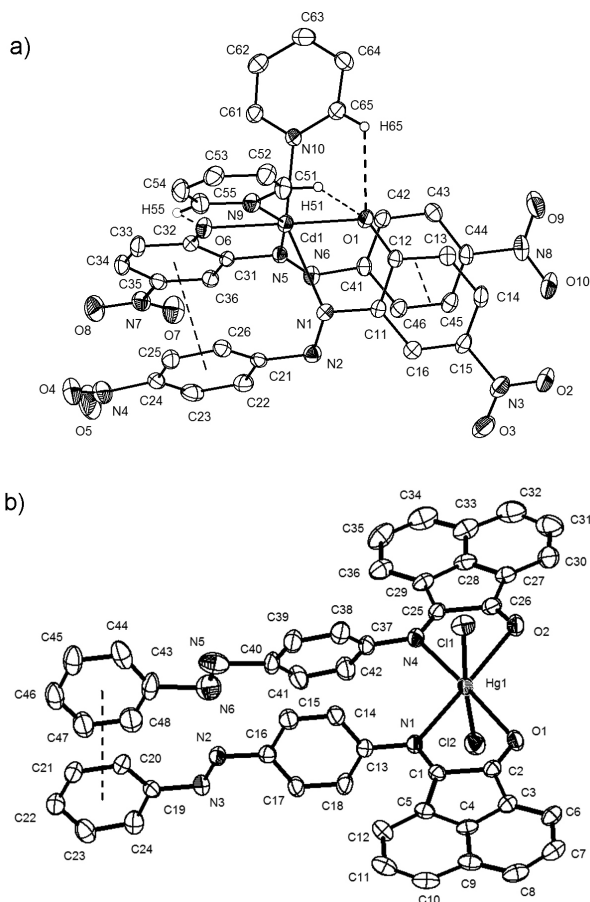


Figure 1. The molecules of (a) **1** and (b) **2**. Ellipsoids are drawn at the 20% probability level and the hydrogen atoms participating in intramolecular C–H···O hydrogen bonds in **1**, but otherwise omitted for clarity, are shown as small spheres of arbitrary radii. Dashed lines represent the C–H···O hydrogen bonds in **1** or, in both cases, π - π interactions.

is the acceptor of two hydrogen bonds, as C51–H51···O1 and C65–H65···O1 (Figure 1a). Additional intramolecular π - π interactions are observed between the phenyl rings of the ligands, whose distances are shown in Table 3. A 1-D network formed along the diagonal of the (101) plane by the C23–H23···O10[#] interaction [symmetry code (#) = $-0.5+x, -0.5-y, -0.5+z$] and the 2₁ screw axis is parallel to the *b* axis and relates all molecules by symmetry (Figure 2). Non-classical H bonds were calculated using the WinGX¹⁷ and PLATON²⁷ programs, and agree with several cases in biological situations described in the literature.^{28,29} All parameters for non-classical H bonds are listed in Table 4.

The crystal structure of **2** shows Hg coordinated to the N and O atoms of the α -iminoketones, as well as to two Cl⁻ ions, as shown in Figure 1b. The observed geometry is that of a distorted octahedron, as can be verified by the angles, which agree with values already found by us in other α -iminoketones.^{30,31} All the pertinent distances and angles can be seen in Table 2. Complex **2** shows Hg–Cl bonds which are shorter than the Hg–N or Hg–O bonds,

Table 2. Selected geometric parameters (Å, °) for **1** and **2**

Bond lengths		Bond angles	
1			
Cd1–N1	2.530(4)	N2–N1–C11	114.6(4)
Cd1–N5	2.630(4)	C21–N2–N1	114.6(4)
Cd1–N9	2.367(4)	N5–N6–C41	113.4(4)
Cd1–N10	2.373(4)	C31–N5–N6	117.0(4)
Cd1–O1	2.247(3)	O1–Cd1–N1	70.34(12)
Cd1–O6	2.221(3)	O6–Cd1–N5	69.19(12)
N1–N2	1.276(5)	O6–Cd1–O1	175.91(12)
N5–N6	1.269(5)	N10–Cd1–N1	145.63(12)
N1–C11	1.422(5)	N9–Cd1–N5	154.73(12)
N2–C21	1.428(5)	N9–Cd1–N10	96.80(13)
N5–C31	1.414(5)		
N6–C41	1.430(5)		
2			
Hg1–N1	2.681(5)	O1–C2–C1	125.0(6)
Hg1–N4	2.662(6)	C1–N1–C13	119.5(6)
Hg1–O1	2.715(4)	O2–C26–C25	123.7 (7)
Hg1–O2	2.811(5)	C25–N4–C37	121.8 (6)
Hg1–Cl1	2.331(2)	Cl1–Hg1–Cl2	174.17(8)
Hg1–Cl2	2.331(2)	N4–Hg1–N1	115.32(18)
C1–N1	1.260(8)	N1–Hg1–O1	64.1(2)
C2–O1	1.202(7)	N4–Hg1–O2	62.7(2)
N4–C25	1.287(9)		
C26–O2	1.225(9)		

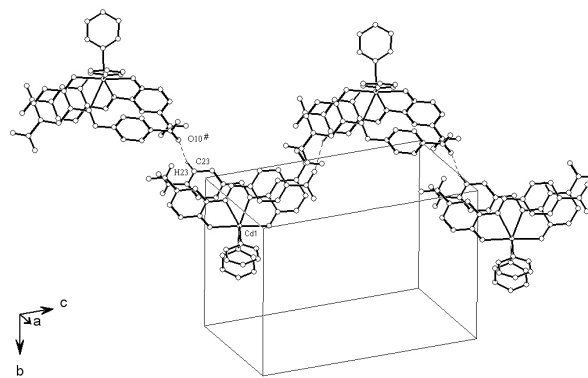


Figure 2. View of the zig-zag one-dimensional self-arrangement cemented by C–H···O non-classical H bonds in **1** [symmetry code (#) = $-0.5+x, -0.5-y, -0.5+z$].

as can be seen from Table 2. This is probably due to steric hindrance between the two azo-containing fragments, as can be seen in Figure 1b. This hindrance prevents the Hg atom to be too close to either N or O. The same effect has been observed in other instances in complexes recently prepared by us and still under study.

In contrast to **1**, **2** does not coordinate through the azo group, showing that the electron-donating sites of the α -iminoketone are more basic than the azo N atoms. The two α -iminoketones coordinated to the metal in **2** are in the *cis* conformation in the equatorial plane. This was an unexpected result, insofar as two bulky groups are located next to each other in the complex molecule. In this conformation the O atoms are located opposite to the N atoms in the equatorial plane. However, if one examines the terminal aromatic rings on the azo groups, one also finds that they present intramolecular π - π interactions,^{32,33} which explains the configuration of the complex. The distances between the centroids in these aromatic rings are shown in Table 3. Figure 1b also presents these interactions. There occur examples in the literature⁹ of complexes with α -iminoketones in which the substituents on the imine nitrogen are alkyl groups, with the N atoms (and also the O atoms) coordinated to the metal in *trans*, unlike the situation observed here. This observation reinforces the idea that the intramolecular π - π interactions present in **2** are the chief causes of the observed configuration. These terminal aromatic rings present a dihedral angle of $7.20(1)^\circ$, as shown by Figure 1b. This slight deviation from planarity is an added indication of an η^6 interaction between the C19-C24

and C43-C48 aromatic rings, showing that they are almost parallel. On the other hand the aromatic rings on the imine nitrogens show a greater dihedral angle of $30.78(1)^\circ$, leading to no appreciable π - π interactions between them, as can be seen in Figure 1b. The acenaphthene rings present a dihedral angle of $9.36(1)^\circ$ with the plane formed by N1-N2-O2-O1-Hg, and the Hg atom is only 0.042 \AA from the plane formed by the N1-N2-O2-O1 atoms.

An analysis of the supramolecular arrangement of **2** shows the formation of a dimer with an inversion center

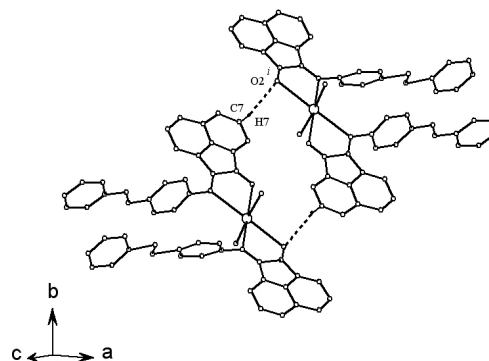


Figure 3. View of the dimer of **2** forming a *teuton* with C-H...O weak interactions [symmetry code (*i*) = $2-x, 2-y, -z$].

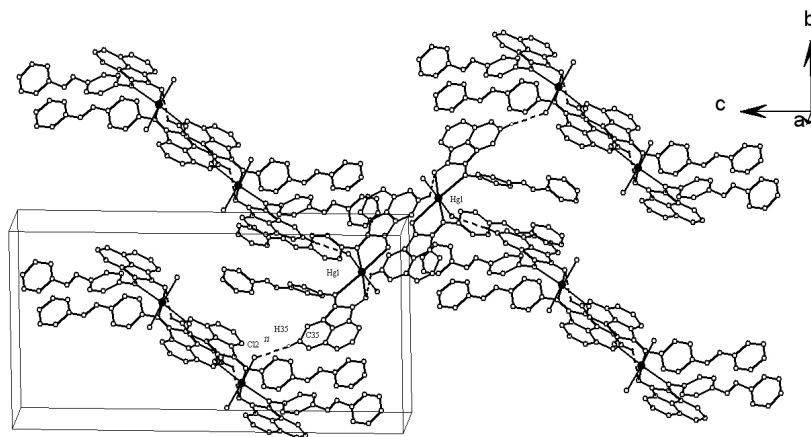


Figure 4. View of the bidimensional self-arrangement of **2** formed by *teuton*s and cemented by C-H...Cl non-classical H bonds [symmetry code (*ii*) = $2.5-x, -0.5+y, 0.5-z$].

Table 3. Parameters (\AA , $^\circ$) for intramolecular π - π interactions in **1** and **2**

Compound	Cg(I)⋯Cg(J)	Cg⋯Cg	α	β	γ	CgI _{perp}	CgJ _{perp}	Slippage
1	Cg(1)⋯Cg(4)	3.533(3)	2.88	19.49	18.40	3.352	3.331	1.147
1	Cg(2)⋯Cg(3)	3.622(3)	8.36	15.15	20.93	3.384	3.497	1.122
2	Cg(1)⋯Cg(2)	3.906(6)	7.20	7.57	13.44	3.800	3.872	0.712

For **1**, Cg(*n*) is the centroid of the ring defined by C(*n*1)-C(*n*6). For **2** Cg(1) and Cg(2) are the centroids of the rings defined by C(19)-C(24) and C(43)-C(48), respectively. Alpha is the dihedral angle between planes I and J. Beta is the angle between Cg(I)⋯Cg(J) and Cg(I)_{perp}. Gamma is the angle between Cg(I)⋯Cg(J) and Cg(J)_{perp}. Cg⋯Cg is the distance between ring centroids. Cg(I)_{perp} is the perpendicular distance of Cg(I) on ring J. Cg(J)_{perp} is the perpendicular distance of Cg(J) on ring I. Slippage is the distance between Cg(I) and the perpendicular projection of Cg(J) on ring I, expressed as an average value when α is non-zero and Cg(I)_{perp} and Cg(J)_{perp} differ.

formed by C7–H7 \cdots O2ⁱ interactions, which are at the limit between van der Waals interactions and non-classical hydrogen bonds, as shown in Figure 3 [symmetry (*i*) = 2-*x*, 2-*y*, -*z*]. Clusters of these dimers form *tectons*^{34,36} using non-classical C35–H35 \cdots Cl2ⁱⁱ hydrogen bond interactions along the (011) diagonal, creating a bidimensional network which can be seen in Figure 4 [symmetry code; (*ii*) = 2.5-*x*, -0.5+*y*, 0.5-*z*]. All the geometric parameters of these interactions are listed in Table 4.

Table 4. Geometric parameters for weak interactions in **1** and **2** in Å (\angle in °)

1				
D-H \cdots A	D-H	H \cdots A	D \cdots A	\angle D-H \cdots A
C23-H23 \cdots O10 [#]	0.93	2.56	3.413(7)	153
C55-H55 \cdots O6	0.93	2.50	3.122(7)	124
C51-H51 \cdots O1	0.93	2.58	3.232(7)	128
C65-H65 \cdots O1	0.93	2.59	3.240(6)	127
2				
D-H \cdots A	D-H	H \cdots A	D \cdots A	\angle D-H \cdots A
C7-H7 \cdots O2 ⁱ	0.93	2.63	3.252(1)	124
C35-H35 \cdots Cl2 ⁱⁱ	0.93	2.77	3.694(2)	172

[symmetry code (#) = -0.5+*x*, -0.5-*y*, -0.5+*z*; (*i*) = 2-*x*, 2-*y*, -*z*; (*ii*) = 2.5-*x*, -0.5+*y*, 0.5-*z*].

Conclusions

This work led to the synthesis and characterization by different methods of two related but wholly different complexes which illustrate a series of important features, both in terms of classical coordination chemistry and in the area of weak, non-classical intra- and intermolecular interactions. Whereas complex **1** is a classical azophenolate chelate complex, **2** is the first azoimineketone complex to appear in the literature. In addition, **2** forms interesting tectons as a result of the weak interactions evidenced by this research. Although azo groups are known to be efficient coordinating groups, as in **1**, the presence of other donor groups in the ligand can lead to different coordination schemes, as shown in **2**. Both complexes show *N,O* coordination, but from different functional groups. The importance of π - π intramolecular interactions cannot be underestimated in both **1** and **2**. 1D and 2D supramolecular arrangements result from C–H \cdots O and C–H \cdots Cl interactions, some of which are clearly non-classical hydrogen bonds. All these interactions are determinant in the structural arrangement of the complexes.

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Supplementary Information

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 667674 and 746970. Copies of the data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or e-mail: deposit@ccdc.cam.ac.uk).

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