

Coordination properties of 2-aminocyclopentene-1-dithiocarboxylic acid to transition metal ions as studied by ab initio calculations

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Abstract

The question of the (*N,S*) vs. (*S,S*) coordination mode on $M \cdot (ACDA)_2$ complexes ($ACDA = 2\text{-aminocyclopentene-1-dithiocarboxylic acid}$, $M = Ni^{2+}, Pd^{2+}, Pt^{2+}$) was assessed through an extensive ab initio study, using the hybrid B3LYP density functional approach. The (*S,S*) coordination was found to be the most stable one, with an energy difference of ca. 50 kJ mol^{-1} relative to the (*N,S*) coordination mode. Detailed analysis of the ab initio results indicates that this preference is a result of the combined effect of geometry constraints and electron distribution within the complex.

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1. Introduction

Metal complexes, in particular of transition metal ions, are important in many areas of science, including catalysis, medicine (diagnosis and therapy), design of high value materials, analytical chemistry and as model compounds of the structure and function of metallo-proteins [1–4]. The metal oxidation state, the type and number of donor atoms, as well as their relative disposition within the ligand are major factors determining structure–activity relationship of the metal complexes. Among the several properties that characterize transition metal complexes of hetero-donor ligands, donor-atom preference profiles and linkage isomerism are promising fields as they offer the possibility of rationally control the activity of bioactive molecules, namely of

enzymes and drugs and/or create molecular devices with tailored properties [5,6].

The metal complexes of 2-aminocyclopentene-1-dithiocarboxylic acid (ACDA) and of some of its *N*- and *S*-alkyl derivatives have received considerable attention [7–23]. This interest was mainly related to the antifungal behavior, ascribed to some transition metal complexes of ACDA [24], but different applications have been found for its coordination properties. For instance, it has been suggested to be an excellent carrier for selective transport of Cu(II) ions [21] and its metal complexes have been used as model compounds of redox-active enzymes [16]. Moreover, it has been used for the simultaneous spectrophotometric determination of iron, nickel and cobalt ions [22]. The ion exchange properties of ACDA chemically bound to silica have also been investigated [15].

Despite this interest, the coordination chemistry of ACDA remains poorly understood. This stands particularly in what concerns the coordination sites, (*N,S*) vs. (*S,S*), and the relative coordination geometry of the ligands in the bis-ligand complexes, either *cis* or *trans* [8,9,18]. To the best of our knowledge, only a single

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crystallographic study on $\text{Co(II)} \cdot (\text{ACDA})_3$ complex has been reported [11], for which a (S, S) coordination mode was observed. A second crystallographic study claims the same coordination but in a bismuth(II) *tris*-complex of an ACDA derivative [12].

Based on spectroscopic studies, Pattnaik and Sen [25] and Nag and Joardar [8] separately claimed a (N, S) coordination mode for the complexes of Ni(II), Pd(II) and Pt(II). More recently, however, the Raman evidences reported by Cappa de Oliveira and Santos [18] suggest in turn a (S, S) coordination mode for the same metal complexes. In addition to this controversy is the fact that, depending on the preparation procedure, more than one differently colored complex, with the same molecular composition, has been obtained for each metal ion [8,18]. This observation has been tentatively correlated with different geometrical isomers (*cis/trans*) of the same complex [8,18].

The present work reports an extensive *ab initio* study on the square planar complexes of Ni(II), Pd(II) and Pt(II) with ACDA, aiming at the understanding of the coordination preferences in these metal chelates and the clarification of the experimental observations of the literature. Several minima were considered for both the free ligand and the metal complexes. The most relevant contributions to structure stabilization were identified on the light of the geometrical parameters and electronic density distribution determined for the minimum energy structures.

2. Computational methods

Density functional theory (DFT) calculations were performed using the Gaussian 98w program (G98w) [26] adapted to a personal computer. The functional used throughout this study consists of a mixture of (Hartree–Fock) HF and DFT exchange functionals and the gradient-corrected correlation functional of Lee, Yang and Parr [27], as proposed and parameterized by Becke [28] (standard B3LYP option of G98w).

For the free ligand, two all-electron basis sets, namely the 6-31G* and the 3-21G(NS)* (3-21G augmented with a polarization function at both nitrogen ($\zeta_{\text{N}} = 0.8$) and sulfur atoms ($\zeta_{\text{S}} = 0.75$) [29]) were used. Each of the four main tautomeric forms shown in Fig. 1 splits into different geometries due to the different relative orientations allowed to both amino and dithiocarboxylic groups, and a total of 19 different geometries were tested and fully optimized. From the initial 19 forms, only 11 were found to be true minima (no imaginary vibrational frequency) at both 6-31G* and 3-21G(NS)*.

In the case of the $\text{M} \cdot (\text{ACDA})_2$ complexes ($\text{M} = \text{Ni}^{2+}$, Pd^{2+} and Pt^{2+}) the 3-21G(NS)* basis set was used on the ligand molecules, while the effective core potential (ECP) and valence basis set of Hay and Wadt [30] (as

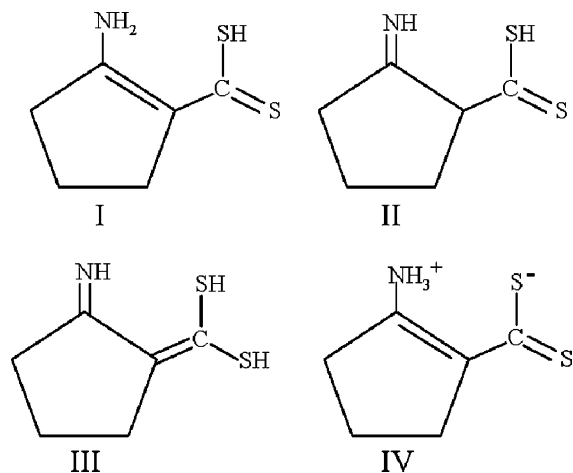


Fig. 1. Main tautomeric forms of 2-aminocyclopentene-1-dithiocarboxylic acid (ACDA).

implemented in G98W) were used to describe the transition metal atoms. These ECPs include the outermost core electrons in the valence shell, incorporate the mass-velocity and Darwin relativistic effects into the potentials for palladium and platinum, and have proven to yield good results for other complexes of the same metals [30–33]. The valence basis set was augmented with an f-polarization function ($\zeta_{\text{Ni}} = 3.130$, $\zeta_{\text{Pd}} = 1.472$ and $\zeta_{\text{Pt}} = 0.993$ [34]).

Each ACDA molecule in a bis-ligand complex can attach to the metal ion via two coordination modes, either (N, S) or (S, S) . Considering the strong bias of Ni(II), Pd(II) and Pt(II) metal ions towards a square planar coordination, three main coordination sets are possible for the $\text{M} \cdot (\text{ACDA})_2$ complexes: $(S, S)(S, S)$ (hereafter named as *bis*- (S, S)), $(S, S)(N, S)$ and $(N, S)(N, S)$ (hereafter named as *bis*- (N, S)). For each of these chelation modes there are two relative orientations of the two ligand molecules within the complex, yielding either the *cis* or the *trans* isomer. In the case of the *bis*- (N, S) coordination, the two cyclopentene rings can be orientated either to the same or to the opposite side of the coordination plane, as schematized in Fig. 2. Moreover, the mutual twisting of the two cyclopentene ring in the bis-complexes duplicates the number of

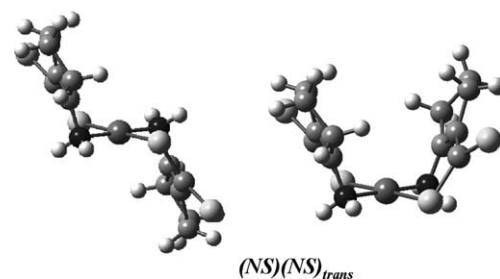


Fig. 2. Possible orientation of the two cyclopentene rings in the bis- (N, S) coordination mode (*trans* isomer is shown).

starting geometries for each metal ion. All the possibilities were considered and fully optimized.

The harmonic vibrational wavenumbers were calculated analytically for all optimized geometries to confirm their convergence to true minimum on the potential-energy surface and to evaluate the zero-point vibrational energy (ZPVE) contribution.

Natural bond orbital (NBO) analyses [35], as implemented in G98w, were performed to obtain a deeper insight into the electronic structure of the optimized geometries. Particular attention was given to natural charges and Wiberg bond orders [35–37].

3. Results and discussion

3.1. Energetic and structural analysis

3.1.1. The free ligand

Fig. 3 presents the lowest-energy minimum obtained for both ACDA and ACDA anion at the 6-31G* theory level. The differences between the 6-31G* and 3-21G(NS)* results are not significant. The atom numbering used throughout the text and tables is included.

On starting with the ACDA species, the calculations are unanimous in predicting tautomer I as the lowest energy form. Other low-lying minima correspond to different geometries based on tautomer I, which differ on the relative orientation of the atoms within the dithiocarboxylic group. The remaining tautomers were found to be less stable by more than 50 kJ mol⁻¹.

The calculations predict a extended delocalization of the π -system over the N–C=C–C=S framework (evident from the bond lengths and bond orders, as will be discussed later), in accordance with experimental results of Cappa de Oliveira et al. [18]. Thus, the highest stability of ACDA is achieved when the two substituents (amino

and dithiocarboxylic groups) and the C₍₁₎–C₍₂₎ double bond of the cyclopentene ring are coplanar. The amino group loses its pyramidal geometry, becoming planar. However, the cyclopentene ring is considerably twisted around the C₍₁₎C₍₅₎–C₍₄₎C₍₃₎ torsional angle (ca. –27° at the 3-21G(NS)* level).

The conjugation of these structural features leads to the formation of two intramolecular hydrogen bonds, which account for significant stabilization of the structure. The coplanarity between the two substituents allows a relatively strong N–H₍₁₎···S hydrogen bond, with H···S distance of ca. 227 and 225 pm, at the 6-31G* and 3-21G(NS)* levels, respectively. The occurrence of such an intramolecular interaction has been predicted experimentally by Bordás et al. [7], who refer the presence of two signals assigned to non-equivalent acidic protons, in the NMR spectra of ACDA. The highest effectiveness of the N–H₍₁₎···S interaction is observed when involving the thiocarbonyl sulfur atom (the structure presenting an N–H₍₁₎···S_(thiol) interaction is predicted to be less stable by more than 28 kJ mol⁻¹, at both theory levels). The second intramolecular hydrogen bond is a C₍₅₎–H···S₍₂₎ interaction, and results from the twisting of the cyclopentene ring. This is a typically weak interaction, with a calculated H···S distance of ca. 278 and 276 pm, at the 6-31G* and 3-21G(NS)* theory levels, respectively.

Upon deprotonation of ACDA, the twisting of the cyclopentene ring around the C₍₁₎C₍₅₎–C₍₄₎C₍₃₎ torsional angle is not affected, but there is a loss of coplanarity between the two substituents and the C₍₁₎–C₍₂₎ double bond. In addition, the amino group recovers its pyramidal geometry. These effects are synchronized in such a way that the N–H···S interaction persists and becomes considerably stronger. Both theory levels predict a considerable shortening of the NH···S distance (by about 6 pm). In contrast, the slight rotation of the dithiocarboxylic group leads to a weakening of the C₍₅₎–H···S₍₂₎ interaction. The H···S distance increases by ca. 3.9 and 1.7 pm, as predicted by 6-31G* and 3-21G(NS)* basis sets, respectively.

3.1.2. The M·(ACDA)₂ (M = Ni²⁺, Pd²⁺ and Pt²⁺) complexes

Fig. 4 displays a graphical view of the relative energies calculated at the 3-21G(N,S)*/LANL2DZ(f) level for the main optimized geometries of each M·(ACDA)₂ (M = Ni²⁺, Pd²⁺, Pt²⁺) complex considered. All geometries were found to correspond to true minima in the potential energy surface.

According to the calculations, both the relative twisting of the two cyclopentene rings nor their orientations relative to the coordination plane in the bis(N,S) geometry set have a significant stability effect and no distinction is made in Fig. 4 for these different orientations of the cyclopentene rings.

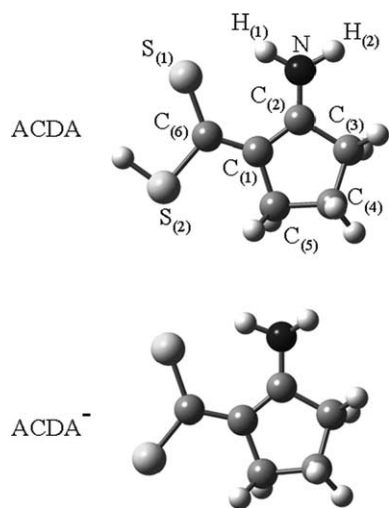


Fig. 3. B3LYP/6-31G* optimized structures and atom numbering, used throughout the text and tables, for ACDA and ACDA⁻ anion.

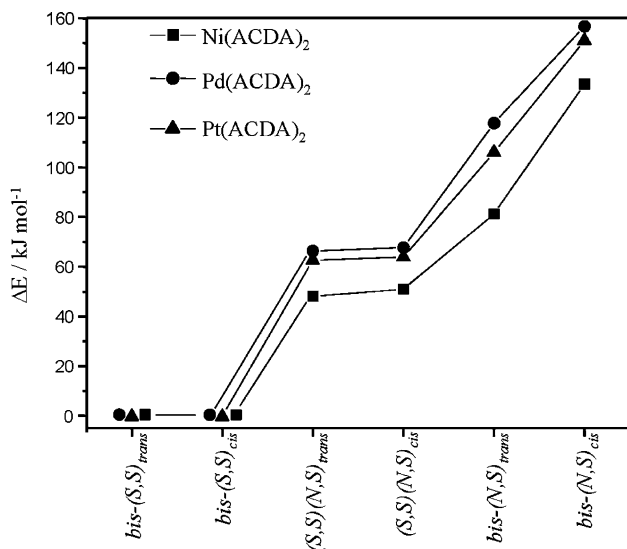


Fig. 4. B3LYP/3-21G(NS)*LANL2DZ(f) energy vs. coordination geometry plot for the $M \cdot (ACDA)_2$ complexes studied.

The calculated results yield a clear preference for the bis-(*S,S*) coordination mode for the three metal ions. The coordination mode stability order is always as follows: bis-(*S,S*) > (*S,S*)(*N,S*) > bis-(*N,S*). An energy gap of 46, 62 and 57 kJ mol⁻¹ was calculated between the bis-(*S,S*)_{trans} and the (*S,S*)(*N,S*)_{trans} structures in the Ni²⁺ and Pd²⁺ and Pt²⁺ complexes, respectively. The energy gap almost duplicates when the bis-(*N,S*) coordination mode is considered (85, 117, 103 kJ mol⁻¹, respectively). The structural distortion imposed to the cyclopentene ring in order to keep the square planar geometry around the coordinated metal ion in a (*N,S*) coordination mode (Fig. 2) arises as one of the main factors determining the stability ordering, as it will be discussed below.

As can be seen in Fig. 4, the type of isomer (*cis* or *trans*) only leads to significant energy differences when the coordination mode is the bis-(*N,S*) one. In this geometry set the calculated *cis/trans* energy gaps for the Ni²⁺, Pd²⁺ and Pt²⁺ complexes are of 42, 28 and 36 kJ mol⁻¹, respectively. For the other two chelation modes the energetic *cis/trans* differences are comparatively small, being almost negligible in the case of the bis-(*S,S*) chelation (1–3 kJ mol⁻¹ and less than 0.3 kJ mol⁻¹, for the (*S,S*)(*N,S*) and bis-(*S,S*) coordination modes, respectively).

The analysis of the predicted energy differences between the above-mentioned forms is conditioned by the nature of the calculations. Ab initio values refer to the isolated molecule and, thus, ignore the intermolecular interactions present in the crystal and in solution. Such intermolecular interactions can easily overcome small conformational energy differences, but are not expected to reverse a clearly defined coordination trend. In fact, the herein reported energy differences undoubtedly suggest

that only the bis-(*S,S*) coordination mode prevail in the $M \cdot (ACDA)_2$ complexes ($M = Ni^{2+}, Pd^{2+}, Pt^{2+}$). On the other hand, the small energy difference found for the *cis* and *trans* isomers reveal that both isomers can coexist in the condensed phases (with proportions dependent on the experimental conditions), thus explaining the observation of slight differently colored complexes with the same molecular formula reported by [8,18].

Table 1 compares some structural parameters calculated at the 3-21G(NS)*LANL2DZ(f) level for the $M \cdot (ACDA)_2$ complexes and for ACDA⁻. For each metal ion only the lowest-energy minimum, the isomer bis-(*S,S*)_{trans}, is included in the table. The values calculated for the protonated species (ACDA) are included for comparison.

Ab initio M–X bond lengths ($M = Ni^{2+}, Pd^{2+}, Pt^{2+}$; $X = S$ or N) were found to be longer than the experimental values of crystal structures [38]. Moreover, DFT bond lengths of second and higher row main-group elements are known to result systematically too large [39,40]. The C–S bond lengths, for instance, are overestimated by about 0.03 Å. Given these limitations, and in the absence of experimental structural data, the herein reported ab initio calculations are a good way to achieve relevant insights into some characteristic structural features of these ACDA metal complexes.

On the whole, the largest structural changes promoted on the ligand molecule by metal coordination to the dithiocarboxylic groups are very similar to those observed on passing from ACDA⁻ to ACDA (protonation process). The only exception occurs in the effect on the two C₍₆₎–S bond lengths. As the metal coordination involves both sulfur atoms, the two C–S bond lengths become almost equal, while protonation (ACDA⁻ → ACDA) leads to a difference between those bond lengths of ca. 10 pm.

In similarity to what is observed upon protonation, no change is predicted for the twisting degree of the cyclopentene rings as a result of metal coordination. The C₍₁₎–C₍₆₎ and C₍₂₎–N distances become significantly shorter, while the C₍₁₎–C₍₂₎ bond length increases. The magnitude of these bond lengths becomes very similar to the values calculated for the ACDA form, and indicates a high degree of π-system delocalization. As a consequence, the NH₂ group loses its pyramidal geometry and the metal coordination plane includes the C₍₁₎–C₍₂₎ bond and the NH₂ and CS₂ groups of both ligands.

On the other hand, metal complexation leads to a significant shortening of the S₍₁₎···S₍₂₎ distances. However, the effect is not systematic on passing from Ni²⁺ to Pd²⁺ to Pt²⁺. In fact, the largest S₍₁₎···S₍₂₎ distance is calculated for the Pd·(ACDA)₂ while the smallest value is predicted to occur for the Pt·(ACDA)₂. A similar distance ordering is also observed for the S₍₁₎···S_(1′) distances (sulfur atoms of different ACDA units occupying a trans position to each other), while the

Table 1

Selected structural parameters calculated at the 3-21G(NS)*/LANL2DZ(f) level for the most stable geometry (bis-(*S,S*)_{trans}) calculated for the M · (ACDA)₂ studied

Structural parameter	ACDA ⁻	ACDA	Ni · (ACDA) ₂	Pd · (ACDA) ₂	Pt · (ACDA) ₂
<i>Bond lengths (pm)</i>					
S ₍₁₎ –C ₍₆₎	173.5	169.0	174.0	174.0	174.1
S ₍₂₎ –C ₍₆₎	171.3	179.3	172.8	172.9	173.0
C ₍₁₎ –C ₍₆₎	146.7	141.4	140.4	140.6	140.5
C ₍₁₎ –C ₍₂₎	137.4	139.8	139.4	139.3	139.3
N–C ₍₂₎	137.5	133.1	133.7	133.8	133.8
N–H ₍₁₎	104.4	103.3	102.3	102.2	102.2
N–H ₍₂₎	102.4	101.6	101.6	101.6	101.6
M–S ₍₁₎	–	–	226.5	239.3	238.4
M–S ₍₂₎	–	–	227.2	239.8	239.5
<i>Bond angles (degrees)</i>					
S ₍₁₎ –C ₍₆₎ –S ₍₂₎	122.2	119.6	110.8	111.5	110.3
S ₍₁₎ –C ₍₆₎ –C ₍₁₎	120.1	126.9	126.2	125.9	126.4
S ₍₂₎ –C ₍₆₎ –C ₍₁₎	117.7	113.5	123.0	122.6	123.3
C ₍₂₎ –C ₍₁₎ –C ₍₆₎	128.7	125.9	127.0	127.1	127.0
N–C ₍₂₎ –C ₍₁₎	129.4	127.7	128.8	128.9	128.8
H ₍₁₎ –N–C ₍₂₎	110.3	117.7	120.3	120.3	120.6
H ₍₂₎ –N–C ₍₂₎	113.8	120.8	120.5	120.4	120.4
S ₍₁₎ –M–S ₍₂₎	–	–	78.0	73.6	73.2
S ₍₁₎ –M–S _(1')	–	–	180.0	179.9	179.9
S ₍₁₎ –M–S _(2')	–	–	102.0	106.4	106.8
<i>Torsional angles (degrees)</i>					
S ₍₁₎ C ₍₆₎ –C ₍₁₎ C ₍₂₎	–4.1	–2.1	±3.0 ^a	–3.7	–3.7
S ₍₂₎ C ₍₆₎ –C ₍₁₎ C ₍₂₎	177.0	177.8	±176.7 ^a	176.1	176.0
NC ₍₂₎ –C ₍₁₎ C ₍₆₎	–6.8	0.5	±0.6 ^a	0.9	0.9
H ₍₁₎ N–C ₍₂₎ C ₍₁₎	14.8	0.6	±0.7 ^a	–1.6	–2.2
H ₍₂₎ N–C ₍₂₎ C ₍₁₎	145.8	179.4	±179.4 ^a	–178.3	–178.0
C ₍₁₎ C ₍₅₎ –C ₍₄₎ C ₍₃₎	–26.4	–26.9	±26.9 ^a	–26.8	–26.7
MS ₍₁₎ –C ₍₆₎ C ₍₁₎	–	–	±178.7 ^a	178.3	178.4
MS ₍₂₎ –C ₍₆₎ C ₍₁₎	–	–	±178.7 ^a	–178.3	–178.5
<i>Non-covalente interactions (pm)</i>					
S ₍₁₎ ···S ₍₂₎	301.9	301.0	285.4	286.8	284.8
S ₍₁₎ ···S _(1')	–	–	453.1	478.6	476.7
S ₍₁₎ ···S _(2')	–	–	352.7	383.7	383.7
NH ₍₁₎ ···S ₍₁₎	219.3	224.8	234.9	235.1	236.1
C ₍₅₎ H···S ₍₂₎	277.4	275.7	293.9	293.0	295.1

The 3-21G(NS)* values calculated for ACDA and ACDA⁻ are included for easier comparison. Atom numbering is in accordance with Fig. 1. ^a ± because the two cyclopentene rings show opposite distortion orientation.

S₍₁₎···S_(2') distances (sulfur atoms of different ACDA units at the same side of the coordination plane) increase according to the metal ordering Ni²⁺ ≪ Pd²⁺ < Pt²⁺. As one would expect, the M–S bond length increases from Ni–S to Pd–S. The Pd–S and Pt–S bond lengths are nearly equal, as was previously found for the dithiolenes of these metal ions [40].

The S₍₁₎–M–S₍₂₎ bond angle decreases from Ni²⁺ (78.0°) to Pd²⁺ (73.6°) and to Pt²⁺ (73.2°). The values of the other S–M–S' (angles involving simultaneously both ACDA units of the complex) show a similar variation pattern as a function of the metal ion. The magnitude of the remaining S–M–S bond angles reflects the preference for the *trans* conformation (S₍₁₎–M–S_(1') and S₍₁₎–M–S_(2') are close to 180° and between 102° and 107°, respectively). Moreover, the magnitude of those bond angles clearly shows a considerable deviation from the

ideal square-planar angle of 90°, with the smallest deviation being observed for the Ni²⁺ complex.

All these structural changes promoted by metal complexation have strong effects on the strength of the intramolecular hydrogen bonding. In fact, the involvement of both sulfur atoms in metal complexation leads to a strong weakening of both intramolecular interactions, and the NH₍₁₎···S₍₁₎ and the CH₍₅₎···S₍₂₎ distances increase by more than 15 pm in the three complexes.

3.2. Natural bond orbital analysis

Natural bond orbital (NBO) analysis yields valuable information concerning the electronic structure of ACDA and its metal complexes. In particular, it allows detailed discussion of the electronic effects determining

the preference of the (*S,S*) coordination over the (*N,S*) one.

Table 2 lists the atomic charges calculated from natural population analysis (NPA) for ACDA⁻, ACDA and the metal complexes with (*S,S*) coordination. The effect of (*S,S*) vs. (*N,S*) coordination modes is illustrated for the Pt·(ACDA)₂ complex. The main effect of the metal coordination – (*S,S*) mode – is the charge transfer from the ligand to the metal center. This is particularly evident for the S-atoms, which loose up to 300 meV, but the electronic flow extends over a significant part of the ligand.

The magnitude of the electron loss at the S atoms increases in the order Ni < Pd < Pt, which is also the order of the positive charge decrease on the metal centers. However, the S atoms contribute only with about one half of the total electron transfer to the metal. Important contributions are also given by the ligand atoms C₍₁₎, C₍₂₎, N and (to a lesser extent) C₍₆₎, all involved in the π -resonance framework. In what concerns the (*N,S*) coordination mode (illustrated in Table 2 for the Pt complex), the situation is quite different. As can be seen from the Pt-metal charges, the electron transfer to the metal is reduced relative to the (*S,S*) mode. Although the electron loss at the S atoms is still significant, part of the electron flow is direct towards the N atom, which acts as an electron acceptor. In addition, the electron flow over the C₍₆₎–C₍₂₎–C₍₁₎ framework is almost frozen out. This charge distribution effects are clearly related with the loss of the π -delocalization upon (*N,S*) coordination, relative to the (*S,S*) coordination.

Additional information concerning the electronic features of ACDA its metal complexes can be obtained from the analysis of the Wiberg bond orders, also provided by the NBO calculations. Fig. 5 presents the Wiberg bond orders calculated for ACDA⁻, ACDA and ACDA bis-metal complexes.

The analysis of the Wiberg bond orders clearly shows the weakening of the C₍₁₎–C₍₂₎ bond upon protonation

of the dithiocarboxylic group and (*S,S*) metal coordination. This effect is slightly stronger in the case of protonation, with the C₍₁₎–C₍₂₎ bond order decreasing from 1.57 to 1.38 and 1.40 upon protonation and metal complexation, respectively. Simultaneously, both N–C₍₂₎ and C₍₁₎–C₍₆₎ bonds become stronger, with the corresponding bonds orders increasing upon both effects (protonation and metal complexation) by ca. 0.14 and 0.15, respectively. Moreover, metal coordination leads to a considerable weakening of the N–H₍₁₎···S₍₁₎ hydrogen bond, in contrast to protonation for which a much smoother effect is predicted.

The comparison of the two coordination modes ((*S,S*) vs. (*N,S*), Fig. 5 – bottom) stresses the trends already derived from the bond order analysis. The (*S,S*) metal coordination mode retains (and even strengthens) the π -delocalization system within the N–C₍₂₎–C₍₁₎–C₍₆₎–S_(1,2) framework observed for the ACDA⁻ anion. In contrast to what is observed in the study of dithiolenes of the same metal ions [40], no change is predicted for the magnitude of the aromatic delocalization as a function of metal ion. In fact, the corresponding bond orders range from a minimum of 1.25 (C₍₆₎–S₍₁₎) to a maximum of 1.40 (C₍₁₎–C₍₂₎) in all the complexes considered. In contrast, the (*N,S*) coordination leads to a pattern of alternating single (C₍₂₎–N, C₍₁₎–C₍₆₎) and double (C₍₁₎–C₍₂₎, C₍₆₎–S₍₂₎) bonds.

An interesting feature is revealed by the ligand–metal bond orders (Fig. 5, central table). Both (*S,S*) and (*N,S*) coordination modes display increasing bond orders following the metal sequence Ni=Pd < Pt (in agreement with the calculated decrease of the metal positive charge). Changing from the (*S,S*) to the (*N,S*) coordination results in a slight increase of the M–S₍₁₎ bond order, while the M–N bond order becomes moderately lower than the replaced M–S₍₂₎ equivalent. These values suggest that the strength of metal–ligand interactions is not the main factor determining the large energy gap between the two coordination modes (*S,S*) and (*N,S*).

Table 2

Atomic charges (*e*) calculated from natural population analysis at the 3-21G(NS)*/LANL2DZ(f) level

Atom	ACDA ⁻	ACDA	Ni·(ACDA) ₂		Pt·(ACDA) ₂	
			bis-(<i>S,S</i>) _{trans}	bis-(<i>S,S</i>) _{trans}	bis-(<i>S,S</i>) _{trans}	bis-(<i>N,S</i>) _{trans}
C ₍₁₎	-0.16	-0.20	-0.20	-0.20	-0.19	-0.07
C ₍₂₎	0.22	0.34	0.30	0.30	0.30	0.19
C ₍₃₎	-0.49	-0.51	-0.51	-0.51	-0.51	-0.50
C ₍₄₎	-0.46	-0.46	-0.46	-0.46	-0.46	-0.46
C ₍₅₎	-0.46	-0.48	-0.47	-0.47	-0.47	-0.47
C ₍₆₎	-0.31	-0.31	-0.29	-0.29	-0.30	-0.36
S ₍₁₎	-0.34	-0.18	-0.16	-0.10	-0.07	-0.10
S ₍₂₎	-0.31	0.06	-0.09	-0.03	-0.01	-0.03
N	-0.80	-0.73	-0.73	-0.73	-0.73	-0.77
H ₍₁₎	0.39	0.42	0.43	0.42	0.42	0.44
H ₍₂₎	0.35	0.40	0.40	0.40	0.40	0.43
(C ₍₅₎)H	0.25	0.26	0.26	0.26	0.26	0.26
M			0.50	0.28	0.18	0.36

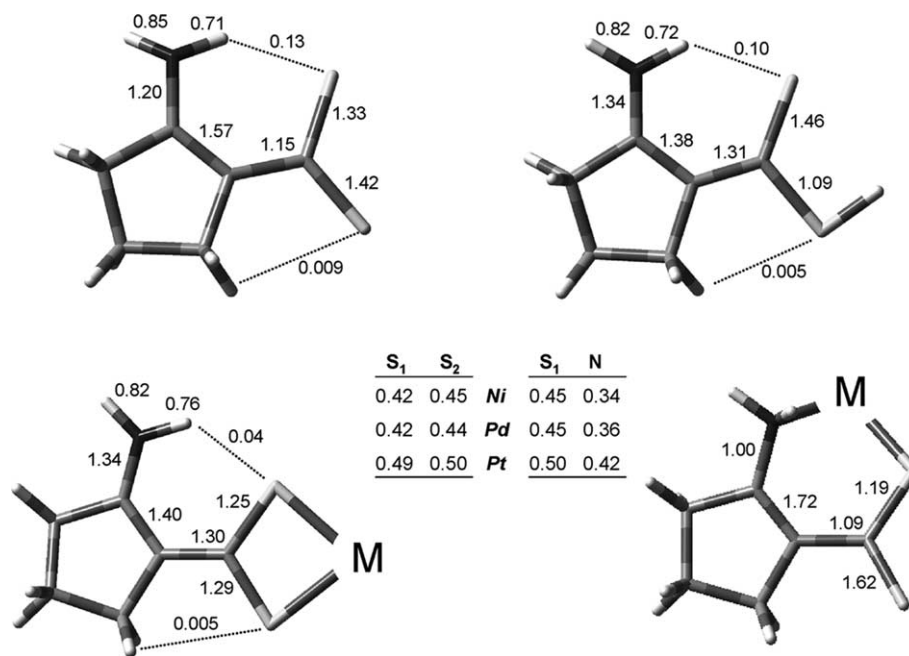


Fig. 5. Selected B3LYP/3-21G(NS)*LANL2DZ(f) NBO bond orders for ACDA, ACDA⁻ anion and metal complexes considered. The bond orders between the metal centers and the donor atoms are shown in the central table.

In fact, it seems that the predicted conformational preference results mainly from the changes occurring within the ligand itself upon metal complexation.

4. Conclusion

The analysis of the energetic and structural parameters of ACDA and its complexes with Ni²⁺, Pd²⁺, and Pt²⁺, complemented with the evaluation of the electronic structure through NBO approach allows the detailed comparison of the (*S,S*) and (*N,S*) chelation modes.

The (*S,S*) coordination mode was found to be preferred by ca. 50 kJ mol⁻¹ on average, as a result of combined geometry constraints and electronic distribution effects. The NBO analysis suggests that the large energy gap obtained between (*S,S*) and (*N,S*) coordination modes do not result mainly from the strength of the metal–ligands contacts, but should be explained by the changes within the ligand itself. In addition, the experimental observation of differently colored species with the same molecular formula is explained by the low energy difference between *cis* and *trans* isomers.

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