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Metal-ligand interactions in transition metal complexes of glyoxilic acid oxime

I. Georgieva, N. Trendafilova*

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev str., bl. 11, 1113 Sofia, Bulgaria

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Dedicated to Acad. Dimiter Ivanov on the occasion of his 120th birth anniversary

The simplest derivative of 2-(hydroxyimino)carboxylic acids, glyoxilic acid oxime (*gaoH*$_2$), was used as a model compound for investigation of the metal-ligand interactions in a series of metal complexes: $Cu(gaoH)_2(H_2O)_2$, $Zn(gaoH)_2(H_2O)_2$, $Co(gaoH)_2(H_2O)_2$, $Ni(gaoH)_2(H_2O)_2$, $[Cd(gaoH)_2(H_2O)_2]H_2O$, K[Pd(gao)(gaoH)] and K[Pt(gao)(gaoH)]3/4H_2O. The coordination abilities of the active ligand forms, $gaoH^{-}$ and gao^{2-}, in gas phase and in solution have been studied and discussed at theoretical level. In agreement with X-ray data for Cu(II), Zn(II), Cd(II), Pt(II) and Pd(II) complexes, the calculations have shown that the most preferred binding is the bidentate one through the carboxylic oxygen and the oxime nitrogen atoms (M-*gaoH*(N,O)). The solvent polarization and the second $gaoH^{-}$ ligand play crucial role for the preferred M-*gaoH*(N,O) binding mode. The nature and the strength of the metal-ligand interactions were estimated in terms of molecular orbital analysis at the DFT(B3LYP/TZVP) level of theory. The largest interaction energy, accompanying by significant net charge transfer from the gao ligand to the metal ion was found for Cu(II) and Pt(II) complexes.

Key words: metal-ligand interactions, transition metal complexes, glyoxilic acid oxime, DFT, ab initio

INTRODUCTION

Glyoxilic acid oxime (*gaoH*$_2$, (H)O-N=C(H)-C(O)-O(H), (IUPAC name: 2-(hydroxyimino)acetic acid)) (oxime analogue of glycine) is the simplest representative of 2-(hydroxyimino)carboxylic acids which exhibit original coordination properties to metal ions. The oxime derivatives are used as suitable matrices for organometallic reactions [1], as very effective complexing agents in the analytical chemistry [2-5], as low temperature precursors for metal oxide ceramic [6] for design and synthesis of magnetic polynuclear assemblies [7] and as model compounds for investigation of metal-protein interactions [8-10]. Metal complexes of *gaoH*$_2$ have also shown versatile bioactivity as chelation therapy agents, drugs, inhibitors of enzymes and as intermediates in the biosynthesis of nitrogen oxide [11,12]. The alternative donor centers of the oxime group (N,O_N) and of the carboxylic group (O,O) lead to many different metal-ligand bindings: monodentate, bidentate chelate (forming four-, five- and six-membered stable rings) and bridging. The O,N-bidentate complexes were found as *cis* [12] and *trans* [13] isomers, the first one being stabilized by hydrogen bonding between the protonated and deprotonated oxime groups. The present work aims to demonstrate the potential of the theoretical methods to gain deeper insight into the coordination properties of the glyoxilic acid oxime to metal ions as well as to estimate the nature and the strength of the metal-ligand interactions in the Zn(II), Cu(II), Ni(II), Co(II), Pt(II) and Pd(II) complexes. The theoretical estimations were done by means of the calculated M-O/N(*gao*) bond lengths, M(II)-*gao* interaction energies, NPA metal charges, M-O/N(*gao*) 2-center Wiberg (Mayer) bond orders (BO), polarization energy contributions, donation and back-donation M↔gao contributions to the bond energy.

RESULTS AND DISCUSSION

Glyoxilic acid oxime is a small molecule with 16 possible conformations which arise from internal rotations around the C–O, C–C, C=N and N–O bonds [14,15]. DFT(BHLYP/6-311G(d,p), B3LYP/6-31++G(d)), HF, MP_n and QCISD(T) calculations have successfully predicted the lowest energy conformer of *gaoH*$_2$, *ectt*, (Fig. 1). Single crystal XRD data confirmed the prediction made and showed that in the solid state four *gaoH*$_2$ molecules in *ectt* conformation are linked by O···H-O and N···H–O hydrogen bonds, forming stable tetramer structure, (Fig. 1) [16]. Vibrational

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* To whom all correspondence should be sent:
E-mail: ntrend@svr.igic.bas.bg

analysis at B3LYP/6-31G(d) level suggested cooperativity in the cyclic H-bonded aggregates in the solid state [17].

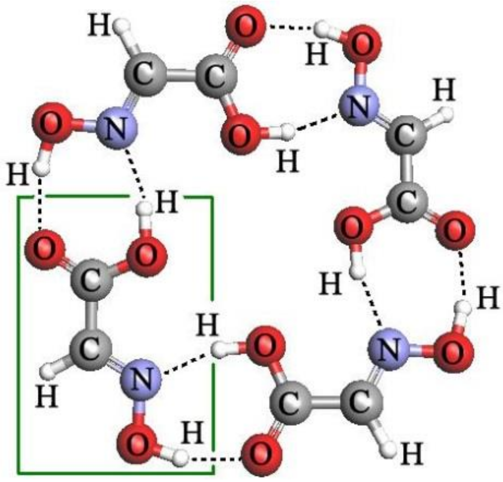
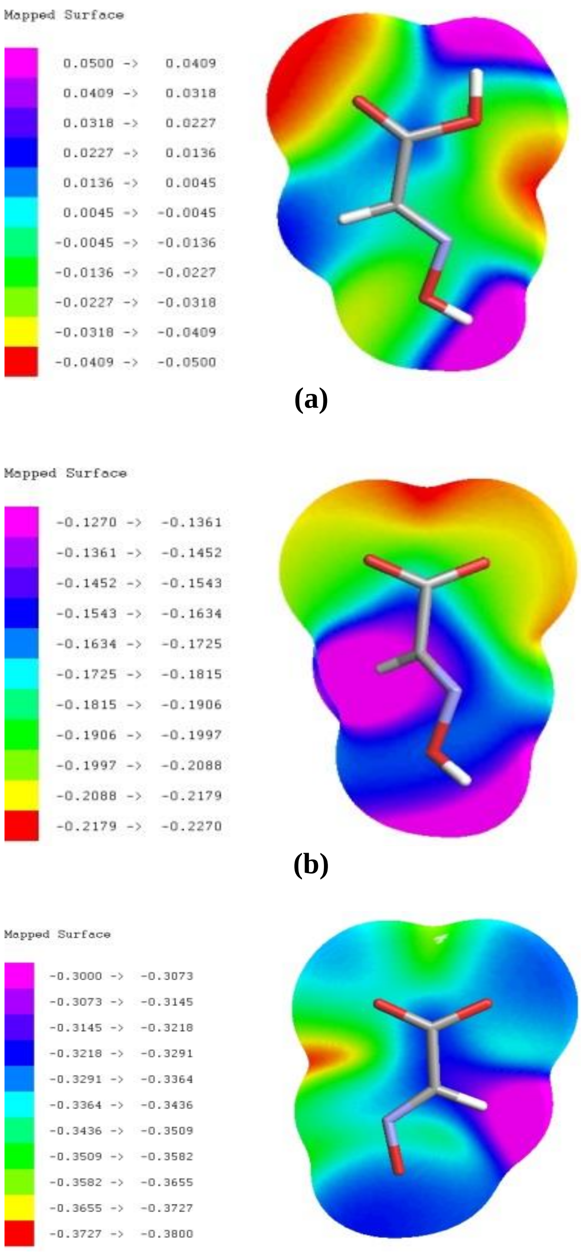


Fig. 1. Cyclic tetramer of glyoxilic acid oxime (*ectt* conformation) with "head-to-tail" bondings, as obtained from single crystal XRD analysis [16]. The lowest energy monomer conformation, *ectt*, is given in a frame.

The most important properties of the glyoxilic acid oxime, however, are revealed in solvent environment. Mono- and doubly deprotonated species of the ligand exist in water solution and they are the active forms of the ligand in complexation reactions with metal ions [15]. O–H bond deprotonation energies (BDE), proton affinity (PA), gas-phase basicity (GB) as well as reactive sites for electrophilic attack were theoretically predicted by detailed comprehensive DFT, MP2 and CCSD(T) studies of $gaoH_2$, $gaoH^-$ and gao^{2-} in gas phase and in solution (SCRF-PCM method) [15]. For the neutral $gaoH_2$, the calculations in solution predicted lower O–H bond deprotonation energy of the COOH group as compared to the NOH group and thus the carboxylic group should firstly be deprotonated in solution [12,13]. The molecular electrostatic potential (MEP) values obtained for $gaoH^-$ and gao^{2-} predicted bidentate coordination to metal(II) ions through both the carboxylic oxygen atoms (O,O) or through the oxime nitrogen and the carboxylic oxygen (N,O) (Fig. 2). The theoretical predictions for the coordination properties of the $gaoH^-$ and gao^{2-} ligand species made on the basis of *ab initio* and DFT computations were proved by experimental studies of Zn(II), Ni(II), Cu(II), Co(II), Cd(II), Pt(II) and Pd(II) complexes of this ligand: single crystal XRD analysis, magnetic measurements, electronic-, NMR-, IR- and Raman spectroscopies [12,13,17,18].



(a)

(b)

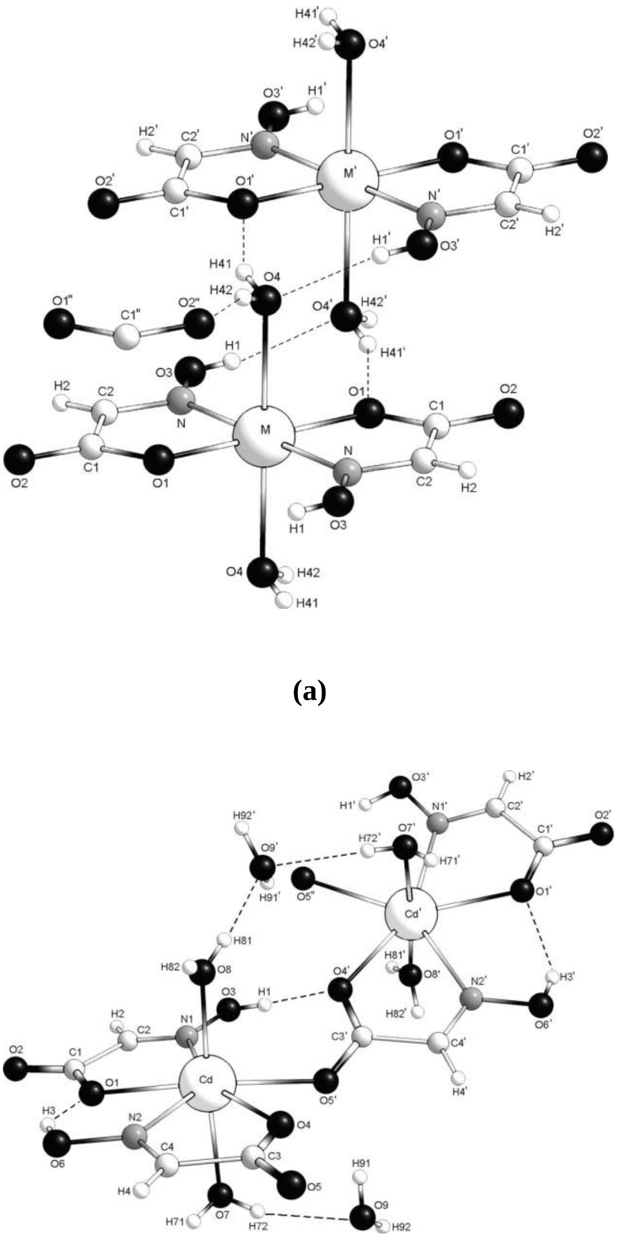
(c)

Fig. 2. Molecular electrostatic potential (MEP) of (a) $gaoH_2$; (b) $gaoH^-$; (c) gao^{2-} species, mapped onto an isosurface of electron density with 0.001 e^{-1}/bohr^3.

Zn(II), Ni(II), Cu(II), Co(II) and Cd(II) complexes of glyoxilic acid oxime

The coordination properties of the deprotonated ligand to Cu(II) were previously studied through calculations of different isomer models for Cu(II):*gao* = 1:1 in gas phase [19]. As a result, a stabilization of the [Cu-$gaoH$(O,O)]$^+$ (bidentate ligand binding through both carboxylic oxygens) was predicted. This finding however does not correspond to the experimentally observed M-L binding mode in the complexes studied, [Cu(*gaoH*(N,O))]$^+$. Therefore, in the present study we extend the theoretical investigation with modeling species Cu(II):gao = 1:2 both in gas phase and in solution. The calculations were performed at DFT(B3LYP/6-31++G(d,p)/6-311++G(d)) levels using the Gaussian09 program package [20]. Two [Cu(*gaoH*)]$^+$, two [Cu(*gaoH*)$_2$] and two [Cu(*gao*)] structures were computed with the most stable anionic and dianionic conformers both in gas phase and in aqueous solution. The calculations of the [Cu(*gaoH*(O,O))]$^+$ and [Cu(*gaoH*(N,O))]$^+$ structures in gas phase predicted more stable [Cu(*gaoH*(O,O))]$^+$ structure by 4.0 kcal/mol. In solution, however, the (N,O) coordination in the [Cu(*gaoH*(N,O)]$^+$ structure is by 6.6 kcal/mol more stable. With addition of a second $gaoH^{-}$ ligand the [Cu(*gaoH*(N,O))$_2$] structure appeared more stable both in the gas phase and in polar solution (by ~11 and 14 kcal/mol, respectively). Obviously, the inclusion of the solvent and of the second $gaoH^{-}$ ligand stabilized the M-*gaoH*(N,O) bidentate binding, which is in agreement with X-ray data obtained for Cu(II), Zn(II), Cd(II) (Fig. 3), Pt(II) and Pd(II) complexes (Fig. 4) [12,13]. In the case of gao^{2-}-Cu(II) coordination mode, the calculations in the gas phase predicted slight stabilization of the [Cu(*gao*(O,O))] structure (by 1.1 kcal/mol) as compared to [Cu(*gao*(N,O))]. In solution, however, the [Cu(*gao*(N,O))] binding appears more stable by 7.6 kcal/mol which is consistent with the experimentally observed gao^{2-}(N,O) coordination realized in the studied complexes [12]. In the Cu(II) and Zn(II) complexes (Fig.3a), the $gaoH^{-}$ ligands form two planar five-membered chelate rings in *trans* position. Two water molecules complete the coordination sphere of the metal atoms taking the axial positions of a distorted octahedron with equal M-O4 bond distances. In the Cd(II) complex of $gaoH^{-}$(Fig. 3b), Cd(II) is seven-coordinated and in addition to the two $gaoH^{-}$(N,O) ligands in *trans* position, the third $gaoH^{-}$ molecule acts simultaneously as bridging (through the COO^{-} group) and chelating ligand (it lies in a plane different from that of the other two $gaoH^{-}$ ligands). Two free coordination sites of the Cd(II) complex are occupied with water molecules which are located above and below the plane of the other two ligands.

Pt(II) and Pd(II) bis-chelate square-planar complexes, K[Pt(*gaoH*)(*gao*)]·3/4H$_2$O and K[Pd(*gaoH*)(*gao*)], have been synthesized and characterized by IR, Raman, NMR and UV-vis spectroscopies as well as by single crystal XRD analysis [12,18].



(a)

(b)

Fig. 3. Molecular structure of: a) M(*gaoH*)$_2$(H$_2$O)$_2$ (M = Cu(II), Zn(II)) and b) [Cd(*gaoH*)$_2$(H$_2$O)$_2$]·H$_2$O, as obtained from X-ray diffraction analysis.

Pt(II) and Pd(II) complexes of glyoxilic acid oxime

Each complex contains one mono- and one doubly deprotonated ligand coordinated to Pt(II) and Pd(II) via the carboxylic oxygen and oxime nitrogen atoms (O,N), forming two *cis*-oriented five-membered planar chelate rings, as shown in Fig. 4. The two ligands are connected via intramolecular hydrogen bond of the N–O···H–O–N type.

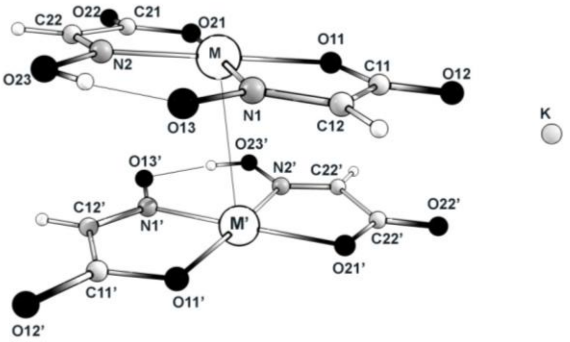


Fig. 4. Molecular structure of *cis*-K[M(*gaoH*)(*gao*)] (M = Pt(II) and Pd(II)), as obtained from X-ray diffraction analysis.

Theoretical estimation of the metal(II)-gao interactions

The molecular structures of complexes studied were optimized at the B3LYP level with 6-311+G(d) basis sets for Co(II), Ni(II), Cu(II), Zn(II), ECPs (SDD) for Pt(II) and Pd(II) and 6-31++G(d,p) for all other atoms. Metal(II)-*gao* interactions in the neutral M(*gaoH*)$_2$(H$_2$O)$_2$ (M = Co, Ni, Cu, Zn) and in the ionic K[M(*gaoH*)(*gao*)] complexes (M = Pd, Pt) were analyzed by means of the calculated M-O/N(*gao*) bond lengths, M(II)-*gao* interaction energies, charge-transfer and polarization energy contributions, donation and back-donation M↔gao contributions to the M(II)-*gao* bond energy (Charge Decomposition Analysis, CDA) [21,22] (in the frame of 2 fragment orbitals calculations), NPA metal charges, M-O/N(*gao*) 2-center (atoms) Wiberg (Mayer) bond order (BO) indices. The CDA and BO components help to analyze the chemical bonding in molecular systems and to monitor changes in the electron density distribution. The CDA approach decomposes the Kohn-Sham determinant of a complex [ML] in terms of fragment orbitals of the ligand, L and the metal [M]. The [M] ← L donation is then given by mixing of the occupied orbitals of L and vacant orbitals of [M]. The [M] → L back-donation is given by the mixing of the occupied orbitals of [M] and vacant orbitals of L. The mixing of the occupied orbitals of both fragments gives the repulsive polarization and the mixing of the unoccupied orbitals - residual term. The 2-center "generalized" Wiberg and Mayer indices, calculated from the canonical MOs in the AO basis resemble the "classical" bond order in diatomic molecule defined as one half of the difference between the number of electrons in the bonding and antibonding states in the corresponding bond. BO value suggests how "strong" the bond is (for single bond the value is close to 1). The Mayer bond orders are:

$$B_{AB} = B_{AB}{}^{\alpha} + B_{AB}{}^{\beta} = 2\sum_{a\in A}\sum_{b\in B}[(P^{\alpha}S)_{ba}(P^{\alpha}S)_{ab} + (P^{\beta}S)_{ba}(P^{\beta}S)_{ab}]$$

where P (P = $P^{\alpha} + P^{\beta}$) and P^{s} ($P^{s} = P^{\alpha} - P^{\beta}$) are the density and spin-density matrices, respectively, P^{α} and P^{β} are α- and β-electron density matrices and S is the overlap matrix. In closed-shell spin-singlet state calculations, $P^{\alpha} = P^{\beta}$, $B_{AB}{}^{\alpha} = B_{AB}{}^{\beta}$ and B_{AB} (Mayer) = B_{AB} (Wiberg). In a general case with $P^{\alpha} \neq P^{\beta}$, the generalized Wiberg and Mayer bond orders are not equal.

The molecular orbital analysis, BO and CDA computations were performed with the B3LYP/TZVP method applying the AOMix program [23,24]. The metal-ligand interactions/bond in the studied metal complexes were estimated in terms of two fragments: M(*gaoH*)(H$_2$O)$_2^+$ (1) and *gaoH*$^-$ (2) for Cu(II), Zn(II), Ni(II) and Co(II) complexes and two types fragments M(*gaoH*)$^+$ (1) and *gaoK*$^-$ (2), and K[M(*gao*)]$^+$ (1) and *gaoH*$^-$ (2) for the Pt(II) and Pd(II) complexes. The two-fragment approach used for Cu(II), Zn(II), Ni(II) and Co(II) complexes better describes the metal-gao bonding in the complexes since it takes into account the perturbation of metal ions by one gao ligand and two water molecules. The results are listed in Table 1 for the Co(II), Ni(II), Cu(II), Zn(II) complexes and in Table 2 for the Pt(II) and Pd(II) complexes.

In keeping with the experimental effective magnetic moments [13], the Co(II), Ni(II) and Cu(II) complexes were calculated in high spin states: multiplicity = 4, 3 and 2, respectively. The calculated bond lengths and bond orders for the neutral Co(II), Ni(II), Cu(II) and Zn(II) complexes (Table 1) predicted a stronger M-O bond than the M-N one. The calculated M-*gao* interaction energy, M-O/N bond lengths, M-O/N bond orders and overlap populations suggested the strongest M-*gao* bonding in the Cu(*gaoH*)$_2$(H$_2$O)$_2$ complex and the weakest one in the high spin Co(*gaoH*)$_2$(H$_2$O)$_2$ complex. The same conclusions were derived by previous analyses of the spectral behavior of ν(COO), ν(M-O) and ν(M-N) frequencies [13]. The charge decomposition analysis results listed in Table 1 showed that at equilibrium Cu-*gao* distance the *gaoH*$^-$ → *Cu*$^+$ donation is the most significant one, 0.846 e (including the largest net charge donation from the ligand to the metal and the electron polarization contribution), whereas the back-donation *Cu*$^+$ → *gaoH*$^-$ is very small. The cal-

Table 1. NBO and CDA data for neutral $\mathrm{M}(gaoH)_2(\mathrm{H_2O})_2$ complexes (M = Co(II), Ni(II), Cu(II), Zn(II))*

Complex	**$R_{\text{M-gao}}$ (Å)**	**q_M (a.u.)**	**E (kcal/mol)**	**BO (a.u.)**	**overlap population**		**Electronic polarization PL(1)-PL(2)**	**Net charge donation CT(2→1)-CT(1→2)**	**d**	**b**	**r**
					α	**β**					
$\mathrm{Co}(gaoH)_2(\mathrm{H_2O})_2$	$1.997^{\text{M-O}}$ $2.120^{\text{M-N}}$ $2.268^{\text{M-Ow}}$	0.97	-181.3/ -651.4^{t}	0.503 0.343 0.199	0.140 0.087 0.053	0.205 0.158 0.096	0.053	0.529	0.681	-0.021	-0.272
$\mathrm{Ni}(gaoH)_2(\mathrm{H_2O})_2$	$2.003^{\text{M-O}}$ $2.047^{\text{M-N}}$ $2.191^{\text{M-Ow}}$	0.90	-182.6/ -674.4^{t}	0.476 0.413 0.237	0.136 0.119 0.061	0.193 0.186 0.114	0.063	0.564	0.712	-0.011	-0.279
$\mathrm{Cu}(gaoH)_2(\mathrm{H_2O})_2$	$1.944^{\text{M-O}}/1.944^{exp}$ $1.981^{\text{M-N}}/2.063^{exp}$ $2.598^{\text{M-Ow}}$	0.96	-191.4/ -691.8^{t}	0.579 0.510 0.031	0.160 0.132 0.016	0.207 0.218 0.013	0.123	0.788	0.846	-0.030	-0.258
$\mathrm{Zn}(gaoH)_2(\mathrm{H_2O})_2$	$1.983^{\text{M-O}}/2.042^{exp}$ $2.175^{\text{M-N}}/2.178^{exp}$ $2.319^{\text{M-Ow}}$	1.21	-182.7/ -653.2^{t}	0.475 0.286 0.156	0.183 0.111 0.065	0.183 0.111 0.065	0.019	0.508	0.683	-0.026	-0.214

*Geometry optimizations - at B3LYP/6-31++G(d,p)/6-311+G(d) level (the latter for Co(II), Ni(II), Cu(II), Zn(II)); population analysis - at B3LYP/TZVP level; BO and CDA calculations with AOMix program. $R_{\text{M-gao}}$ – optimized M-O and M-N bond lengths; q_M - NPA charge of metal ion in the complex; E - interaction energy between $\mathrm{M}(gaoH)(\mathrm{H_2O})_2^+(1)$ - $gaoH^-(2)$ fragments (M=Cu, Zn, Ni, Co); BO- 2-centers Bond Order (Mayer BO – for open shell complexes, Wiberg BO - for closed shell complexes); net charge donation ($gaoH^- \rightarrow \mathrm{M}(gaoH)(\mathrm{H_2O})_2^+$); $gaoH^- \rightarrow \mathrm{M}(gaoH)(\mathrm{H_2O})_2^+$ donation d (including charge donation and electronic polarization); $\mathrm{M}(gaoH)(\mathrm{H_2O})_2^+ \rightarrow gaoH^-$ back-donation b; $\mathrm{M}(gaoH)(\mathrm{H_2O})_2^+ \leftrightarrow gaoH^-$ repulsive polarization r.

Table 2. NBO and CDA data for ionic $\mathrm{K}[\mathrm{M}(gaoH)(gao)]$ complexes (M=Pt(II), Pd(II))[a]

Complex	**$R_{\text{M-gao}}$ (Å)**	**q_M (a.u.)**	**E (kcal/mol)**	**BO (a.u.)**	**overlap population**		**Electronic polarization PL(1)-PL(2)**	**Net charge donation CT(2→1)-CT(1→2)**	**d**	**b**	**r**
					α	**β**					
$\mathrm{K}[\mathrm{Pd}(gaoH)(gao)]$	$2.054^{\text{M-O*}}/2.036^{exp}$ $1.996^{\text{M-N*}}/1.957^{exp}$ $2.054^{\text{M-O**}}/2.021^{exp}$ $1.997^{\text{M-N**}}/\ 1.948^{exp}$	0.62	-191.9* -280.5**	0.512 0.590 0.421 0.608	0.153 0.204 0.105 0.201	0.153 0.204 0.105 0.201	0.033 -0.074	0.657 0.923	0.719 0.781	0.176 -0.017	-0.504 -0.504
$\mathrm{K}[\mathrm{Pt}(gaoH)(gao)]$	$2.069^{\text{M-O*}}$ $1.986^{\text{M-N*}}$ $2.059^{\text{M-O**}}$ $1.994^{\text{M-N**}}$	0.30	-212.3* -298.4**	0.521 0.659 0.457 0.655	0.138 0.176 0.106 0.159	0.138 0.176 0.106 0.159	0.016 -0.096	0.688 0.935	0.728 0.806	0.153 -0.049	-0.624 -0.624

[a] Molecular optimizations are performed at B3LYP/6-31++G(d,p)/SDD level (the latter - for Pt(II) and Pd(II)); population analysis - at B3LYP/TZVP level; WBO and CDA calculations with AOMix program. $R_{\text{M-gao}}$ – optimized M-O and M-N bond lengths; q_M - NPA charge of metal ion in the complex; E* - interaction energy between $\mathrm{M}(gaoH)^+(1)$ - $gaoK^{-}$ (2) fragments, E** - interaction energy between $\mathrm{K}[\mathrm{M}(gao)]^+(1)$ - $gaoH^-$ (2) fragments (M = Pt, Pd); BO- 2-center Bond Order (Wiberg); net charge donation (*$gaoH^- \rightarrow \mathrm{M}(gao)\mathrm{K}^+$ and **$\mathrm{K}gao^{-} \rightarrow \mathrm{M}gaoH^+$); *$gaoH^- \rightarrow \mathrm{M}(gao)\mathrm{K}^+$ and **$\mathrm{K}gao^- \rightarrow \mathrm{M}gaoH^+$ donation d (including charge donation and electronic polarization); *$\mathrm{K}[\mathrm{M}(gao)]^+ \rightarrow gaoH^-$ and **$\mathrm{M}gaoH^+ \rightarrow gao\mathrm{K}^-$ back-donation b; *$\mathrm{K}[\mathrm{M}(gao)]^+ \leftrightarrow gaoH^-$ and **$\mathrm{M}gaoH^+ \leftrightarrow gao\mathrm{K}^-$ repulsive polarization r.

culations revealed that the $gaoH^-$ ligand is a strong donor and a weak acceptor in all the neutral complexes studied.

The calculated M(II)-N/O bond lengths and the corresponding BOs for the ionic Pt(II) and Pd(II) complexes of *gao* predicted stronger M(II)-N bonds than M(II)-O ones which is in contrast to the results obtained for the neutral Co(II), Ni(II), Cu(II) and Zn(II) complexes of *gao*. The interaction energies of Pt(II)-$gaoH^-/gao^{2-}$ are larger as compared to the corresponding Pd(II)-$gaoH^-/gao^{2-}$ ones. More negative interaction energy and stronger metal-ligand bonding (larger donation contribution to the M(II)-gao^{2-} bond energy) were predicted for the metal-dianion binding (Pt(II)/Pd(II)-gao^{2-}) than for the metal-monoanion binding (Pt(II)/Pd(II)-$gaoH^-$).

CONCLUSION

As the simplest derivative of the 2-(hydroxyimino) carboxylic acids the glyoxilic acid oxime is a very suitable model compound for investigation of metal-ligand interactions in transition-metal complexes. The coordination abilities of the active $gaoH^-$ and gao^{2-} forms in solution were predicted by MEP calculations and different metal-ligand bonding isomers. The largest stabilization was found for the structures with M-*gaoH*(N,O) bidentate binding through the carboxylic oxygen and the oxime nitrogen atoms, which is in agreement with X-ray data for Cu(II), Zn(II), Cd(II), Pt(II) and Pd(II) complexes. The solvent polarization and the second $gaoH^-$ ligand play crucial role for the preferred M-*gaoH*(N,O) binding mode. The calculated M(II)-N/O bond lengths and the corresponding bond orders for the ionic Pt(II) and Pd(II) complexes of *gao* predicted a stronger M(II)-N bond than the M(II)-O one, which is in contrast to the results obtained for the Co(II), Ni(II), Cu(II) and Zn(II) neutral complexes of *gao*, where the M(II)-O interaction is stronger than the M(II)-N one. Among the studied neutral transition metal complexes, the largest interaction energy was found for Cu(II)-$(gaoH^{-})_2$ and among the ionic metal complexes, the larger interaction energy is predicted for Pt(II)-$gaoH^{-}/gao^{2-}$. For these complexes, the net charge transfer energy contribution from the *gao* ligand to the metal ion is the largest one in the series of complexes studied.

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МЕТАЛ-ЛИГАНД ВЗАИМОДЕЙСТВИЯ В КОМПЛЕКСИ НА ПРЕХОДНИ МЕТАЛИ С ОКСИМА НА ГЛИОКСИЛОВАТА КИСЕЛИНА

И. Георгиева, Н. Трендафилова*

Институт по обща и неорганична химия, Българска Академия на Науките, ул. Акад. Г. Бончев, бл. 11, 1113 София, България

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(Резюме)

Оксимът на глиоксиловата киселина (*gaoH₂*) е използван като модел за изследване на метал-лиганд взаимодействията в серия комплекси на преходни метали с този лиганд: Cu(*gaoH*)$_2$(H$_2$O)$_2$, Zn(*gaoH*)$_2$(H$_2$O)$_2$, Co(*gaoH*)$_2$(H$_2$O)$_2$, Ni(*gaoH*)$_2$(H$_2$O)$_2$, [Cd(*gaoH*)$_2$(H$_2$O)$_2$]H$_2$O, K[Pt(*gao*)(*gaoH*)]3/4H$_2$O and K[Pd(*gao*)(*gaoH*)]. Координационната способност на активните форми на лиганда, *gaoH*$^-$ и *gao*$^{2-}$, в газова фаза и в разтвор е изследвана на теоретично ниво. В съгласие с рентгеноструктурни данни за комплексите на Cu(II), Zn(II), Cd(II), Pt(II) и Pd(II) изчисленията показват, че най-предпочетеното свързване е бидентатно чрез карбоксилния кислороден атом и азотния атом от оксимната група, M-*gaoH*(N,O). Установено е, че ефектът на полярния разтворител и присъствието на втори лиганд в молекулата имат определяща роля при реализиране на свързването M-*gaoH*(N,O). Природата и силата на метал-лиганд взаимодействията в изследваните комплекси са оценени чрез МО изчисления на DFT(B3LYP/TZVP) ниво на теорията. Най-голяма стойност на енергията на взаимодействие и най-голям пренос на заряд от лиганда към металния йон е намерен за комплексите на Cu(II) и Pt(II).