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Article

Are Chelate Rings Aromatic? Calculations of Magnetic Properties of Acetylacetonato and *o*-Benzoquinonediimine Chelate Rings

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The aromaticity of the chelate rings of acetylacetonato (acac) and *o*-benzoquinonediimine (bqdi) ligands was investigated theoretically by calculating nucleus-independent chemical shifts (NICS). The calculations were done for the complexes with various metals and various other ligands. The results show that acac chelate rings in none of the complexes satisfy this magnetic criterion for aromaticity. According to the results for bqdi chelate rings, there is only the Ru^{2+}–bqdi chelate ring with large negative NICS values, indicating possible aromaticity by magnetic criterion.

Introduction

The idea of aromaticity of chelate rings was introduced by Calvin and Wilson.[1] The importance of metalloaromaticity for the better understanding of the degree of communication between the metal centers of multinuclear complexes has been stressed repeatedly in many fields from biological electron-transfer processes to solving technological problems such as the harvesting of light energy. Metalloaromaticity stabilizes coordinated chelate ligands, allows electrophilic substitution reaction to take place on the ligand, affects π-electron distribution, and allows charge-transfer complexes to form with chelates. Furthermore, both spectroscopic and magnetic properties of these complexes are affected by the degree of the aromaticity.[2]

Metalloaromaticity has been studied by variety of experimental and theoretical methods.[3−7] Initially, there was

assumption that many chelate rings can be aromatic. However, numerous claims of aromaticity in the metal chelates of α,β-diketones were disputed by Holm and Cotton.[8] Kuhr et al.[9] measured the diamagnetic anisotropy in the acetylacetonato chelate rings and reported small anisotropies. On the other hand, Häfelinger et al.[10] showed that there are large anisotropies in transition metal α,α′-diimine complexes. A

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survey of the literature in which the transition metal chelates containing α,α'- or α,β-unsaturated fragments are said to have aromatic qualities or appear to have a high degree of delocalization around the chelate ring is summarized in Masui's review paper.[2]

Interest in noncovalent interactions with aromatic rings, such as CH/π, cation-π, and stacking,[11] prompted studies of noncovalent interactions with a chelate ring as a π-system.[12−17] In these studies it was observed that planar chelate rings with delocalized π-bonds can be involved in the interactions in a manner similar to those in organic aromatic rings, indicating that these chelate rings could have aromatic character.

By a screening of the Cambridge Structural Database (CSD),[18] it was shown that a chelate ring can be a hydrogen
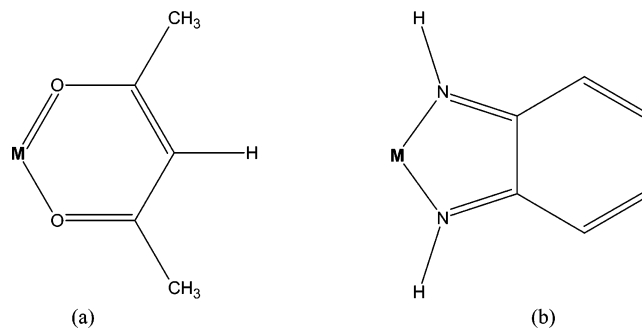

Figure 1. Schematic representations of the M(acac) chelate ring (a) and M(bqdi) chelate ring (b).

atom acceptor in CH/π interactions.[12−14] Both geometries and calculated energies of CH/π interactions of chelate rings[14] are similar to those of the CH/π interaction of benzene.[19] Stacking interactions of chelate rings were found in the crystal structures of transition metal complexes.[15,17] Mutual slipped-parallel (offset face to face) orientation of two rings shows that stacking interaction between phenyl and chelate rings[17] are similar to the stacking interaction of two benzene rings.[19]

The similarity of noncovalent interactions of chelate and benzene rings suggests that these chelate rings could have aromatic character. However, further properties related to the aromaticity of these chelate rings need to be studied. The nucleus-independent chemical shift (NICS) index defined by Schleyer et al.[20] became well accepted as one of the most efficient tools for understanding aromaticity. The NICS(0) value is calculated at the center of the ring, while NICS(1) refers to the location 1.0 Å above the center of the ring. The NICS(0) and NICS(1) values of a typical aromatic system like the benzene ring are around −8 and −10, respectively, depending on the method of calculation. It was shown that NICS values correlate well with other aromatic properties.[21]

A few studies on calculations of NICS values for chelate rings were published.[6,7] For the special case, metallabenzenes, Iron et al. showed that they may be aromatic, as some of them have planar geometries with bond length equalization, molecular orbitals that are akin to those of benzene, and negative NICS values. The NICS(0) and NICS(1) values of iridiabenzene in the $(C_5H_5Ir)(PH_3)_3$ complex are −3.7 and −8.8, respectively.[7]

To further elucidate the metalloaromaticity of the acetylacetonato (acac) (Figure 1a) and o-benzoquinonediimine (bqdi) (Figure 1b) chelate rings, we present here the results on calculations of their NICS values. We chose these chelate rings because of intensive interest in their metalloaromaticity and numerous experimental and theoretical studies related to that interest.[2] To the best of our knowledge, this is the first study presenting NICS values for the acetylacetonato (acac) and o-benzoquinonediimine (bqdi) chelate rings.

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Computational Details

The model systems for calculations were taken from CSD or were obtained by modifying the crystal structures. Since crystal structures sometimes display unrelaxed intramolecular geometries yielding distorted wave functions, we optimized the geometries of chosen metal complexes using the Gaussian 98 program.[22] The geometry optimization was performed using density functional theory (DFT), specifically the Becke three-parameter exchange functional (B3)[23] and the Lee−Yang−Parr correlational functional (LYP).[24] The geometry optimizations of the bis-acac complexes were carried out using the SDD basis set with the Stuttgart−Dresden effective core potential (ECP) on metal atoms for Ni, Pt, Ca, and Mg.[25] For a description of the carbon, hydrogen, and oxygen atoms, the correlation consistent polarized valence double-ζ (cc-pVDZ) basis set developed by Dunning[26] was employed. For optimization of all other complexes, the LANL2DZ[27] basis set was chosen for the metal atom (Ni, Pt, Ru, Os, Rh, and Ir) with the Los Alamos ECP for the core electrons of the metal atoms. For the carbon, hydrogen, oxygen, nitrogen, and fluorine atoms, the 6-31G** basis set was employed.[28]

The magnetic properties of molecules, chemical shifts, and NICS values were calculated using the Gaussian 98 and the deMon *(*density of Montréal*)* program packages.[29] The B3LYP and the Perdew−Wang 91 (PW91) functionals were used in the calculations.[30] To evaluate magnetic properties employing the Gaussian 98 program, the gauge-including atomic orbitals (GIAO) method was used.[31] With this method, three basis set−ECP combinations were used. The first basis set, BS1, includes the above-mentioned SDD on metal atoms and the Dunning's aug-cc-pVDZ basis set on lighter elements.[32] The second basis set, BS2, involves the same combination basis set−ECP as BS1 and additional spdf set of diffuse functions on metal atoms, which is listed in Table S2 of ref 7. (This additional spdf set of diffuse functions on metal atoms with the SDD basis is denoted by aug-SDD.) The third basis set, BS3, consists of the LANL2DZ and 6-31G** basis sets for metal and lighter atoms, respectively.

The individual gauge for localized orbitals (IGLO)[33] approach for solving the gauge problem was also used. With this method the IGLO III basis set[34] for ligand atoms and aug-SDD for metal atom were employed. As well as the orbital basis set, the standard auxiliary function set was employed. The NICS values were calculated with the "dummy" atom suspended either 0.0 Å (NICS-(0)) or 1.0 Å (NICS(1)) above the center of the ring.

To evaluate the influence of basis set and method on NICS values, the calculations for Ni(acac)$_2$ were done with different basis sets (for light atoms aug-cc-pVDZ, IGLO III, and 6-311+G*;[35] for metal atoms SDD, aug-SDD, and Wachters+f[36]) and with different methods (B3LYP, PW91). For solving the gauge problem different approaches (GIAO and IGLO) were employed. The calculated NICS(1) values are similar; they vary from −1.82 to −2.53. Hence, different methods and basis sets have moderate impact on the calculated NICS values. Then, the interpretation of their absolute values has to be taken with caution. However, trends for the rings in the same basis sets should be more accurate than the absolute values.

Results and Discussion

We calculated NICS(0) and NICS(1) values ("dummy" atom suspended either 0.0 Å (NICS(0)) or 1.0 Å (NICS(1)) above the center of the ring) for chelate and benzene rings in a number of transition metal complexes containing acetylacetonato (acac) and *o*-benzoquinonediimine (bqdi) ligands. The calculations were done for complexes with various metals and various other ligands.

Acetylacetonato Chelate Rings. The NICS values were calculated for metal−acetylacetonato chelate rings in square-planar [M(acac)$_2$] complexes of Ni^{2+}, Pt^{2+}, Mg^{2+}, and Ca^{2+} and in [M(acac)(NH$_3$)$_2$]$^+$ complexes of Ni^{2+} and Ca^{2+}. The structures of the complexes are displayed in Figure 2, and

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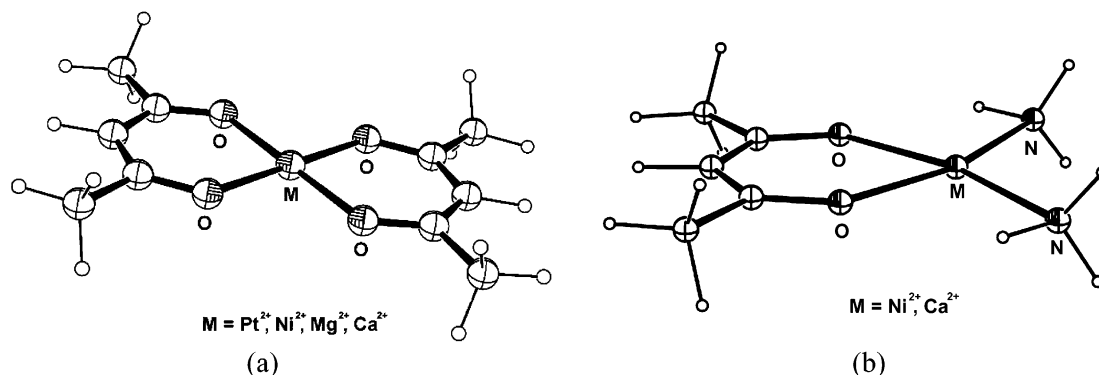**Figure 2.** Molecular diagrams of the [M(acac)$_2$] (M = Pt^{2+}, Ni^{2+}, Mg^{2+}, Ca^{2+}) complexes (a) and of the [M(acac)(NH$_3$)$_2$]$^+$ (M = Ni^{2+}, Ca^{2+}) complexes (b).

Table 1. NICS(x) (x = 0, 1 in ppm) Values Calculated[a] for acac Complexes

complex	NICS(0)	NICS(1)
[Pt(acac)$_2$][b]	−0.95	−1.73
[Ni(acac)$_2$][b]	−3.72	−1.82
[Mg(acac)$_2$][c]	+3.10	+0.16
[Ca(acac)$_2$][c]	+3.30	+0.28
[Ni(acac)(NH$_3$)$_2$]$^+$ [c]	−3.58	−2.23
[Ca(acac)(NH$_3$)$_2$]$^+$ [c]	+3.88	+0.73

[a] In all cases the B3LYP method and the GIAO approach were employed. [b] BS2. [c] BS1.

Table 2. NICS(x) (x = 0, 1 in ppm) Values Calculated[a] for Chelate and Benzene Rings in Complexes with bqdi Ligand

complex	ring	NICS(0)	NICS(1)
[Ni(bqdi)$_2$]$^{2+}$	chelate	−1.25	+0.22
	benzene	+9.35	+3.42
[Pt(bqdi)$_2$]$^{2+}$	chelate	+0.42	−1.17
	benzene	+7.92	+2.35
[Rh(bqdi)$_2$F$_2$]$^+$	chelate	+2.85	−1.22
	benzene	+5.08	+0.07
[Ir(bqdi)$_2$F$_2$]$^+$	chelate	+1.10	−2.54
	benzene	+4.07	−0.66
[Ru(bqdi)$_2$F$_2$]	chelate	−4.93	−7.25
	benzene	−0.74	−4.15
[Os(bqdi)$_2$F$_2$]	chelate	+8.56	+2.90
	benzene	−0.74	−3.33
trans-[Ru(bqdi)(en)F$_2$]	chelate	−8.52	−10.92
	benzene	−7.72	−9.38
cis-[Ru(bqdi)(en)F$_2$]	chelate	−8.83	−10.41/−12.00
	benzene	−7.38	−9.08
[Ru(bqdi)(acac)$_2$]	chelate	−3.29	−7.20
	benzene	−3.90	−6.57
	acac	−0.37	−1.43

[a] BS3 basis set, B3LYP method, and GIAO approach.

the calculated NICS values for the acac chelate rings are presented in Table 1. The NICS(1) values shown in Table 1 vary from −2.23 to +0.73, indicating that the acac chelate rings in these complexes do not satisfy the NICS magnetic criterion for aromaticity. The acac chelate ring is not aromatic in any of these complexes, regardless of the metal and ligands in the complex. Although we did not get significant negative NICS values for any of the acac chelate rings, we obtained different signs for chelates with s- (Mg and Ca) and d-metals (Ni and Pt), which can be anticipated on the basis of the π-bonding capabilities of d-metals.

There is a controversy about aromaticity of metal−acetylacetonato chelate rings. On the basis of the electrophilic aromatic substitution reactions, as one of the properties in which metalloaromaticity is manifested, there is significant intramolecular, interannular communication in some acetylacetonato complexes. However, our results that the acac chelate rings are not aromatic are in agreement with previous experimental results on the ^{1}H NMR spectra of the acac ligands with various metals.[8] In these complexes the chemical shift of the central hydrogen atom from the acac ligand is nearly independent of the nature of the metal ion completing the chelate ring with regard to charge, size, and ability to build π-bond with the ligand system. Holm and Cotton also questioned the validity of the presence of aromaticity in the acac chelate rings on the basis of a charge-transfer spectra of a broad range of metal ion complexes with acac ligands.[8] The ^{1}H NMR chemical shifts of the hydrogen atoms from the covalently bound mesityl and anthryl groups do not show any diamagnetic anisotropy around the acac chelate ring.[9]

***o*-Benzoquinonediimine Ligand.** The magnetic properties of transition metal complexes with the bqdi ligand were investigated in the square-planar (Figure 3a) and octahedral

(Figure 3b) complexes of d^8 and d^6 electronic configurations, respectively. The NICS values calculated for the chelate and benzene rings in number of complexes {[M(bqdi)$_2$]$^{2+}$ (M = Ni^{2+}, Pt^{2+}), [M(bqdi)$_2$F$_2$] (M = Ru^{2+}, Os^{2+}), [M(bqdi)$_2$F$_2$]$^+$ (M = Rh^{3+}, Ir^{3+}), trans- and cis-[Ru(bqdi)(en)F$_2$], [Ru(bqdi)-(acac)$_2$]} are collected in Table 2. In square-planar bis(bqdi) complexes of Ni^{2+} and Pt^{2+}, the NICS values are positive or small negative numbers, indicating that the bqdi chelate is not aromatic. Among investigated octahedral complexes of Ru^{2+}, Os^{2+}, Rh^{3+}, and Ir^{3+}, the complexes of Ru^{2+} are the only complexes with large negative NICS values for the bqdi chelate rings that indicate aromaticity (Table 2). In complexes of other metals, the bqdi chelate rings do not have large negative NICS values. This indicates that only Ru^{2+}, among studied metal ions, could have the properties necessary to form an aromatic ring with bqdi ligand. The loss of the aromaticity of benzene ring in some of the complexes in Table 2 will be discussed latter.

Since there is mutual influence of ligands in metal complexes, the NICS values for the Ru^{2+}−bqdi chelate ring could be affected by other ligands coordinated to the metal. To check the influence of other ligands in the complex on the aromaticity of Ru^{2+}−bqdi chelate ring, calculations of NICS values were done for complexes with acac, fluoro, and
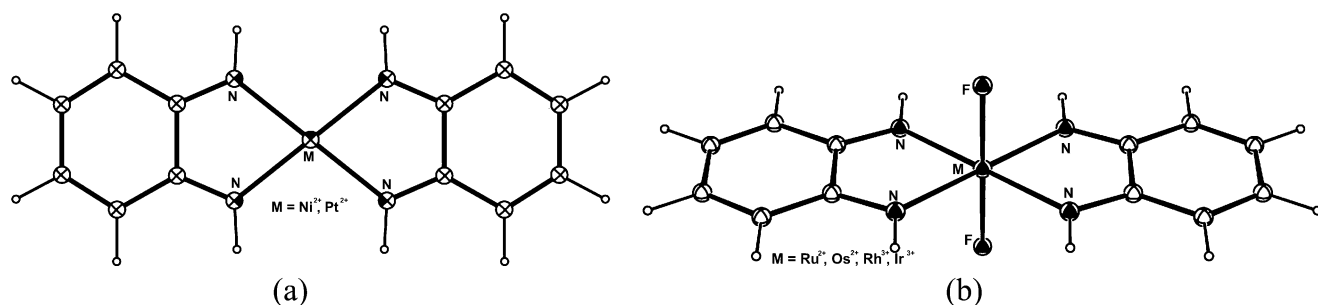
(a)

(b)

Figure 3. Molecular diagrams of the $[M(bqdi)_2]^{2+}$ (M = Ni^{2+}, Pt^{2+}) complexes (a) and $[M(bqdi)_2F_2]$ (M = Ru^{2+}, Os^{2+}) and $[M(bqdi)_2F_2]^+$ (M = Rh^{3+}, Ir^{3+}) complexes (b).

cis

trans

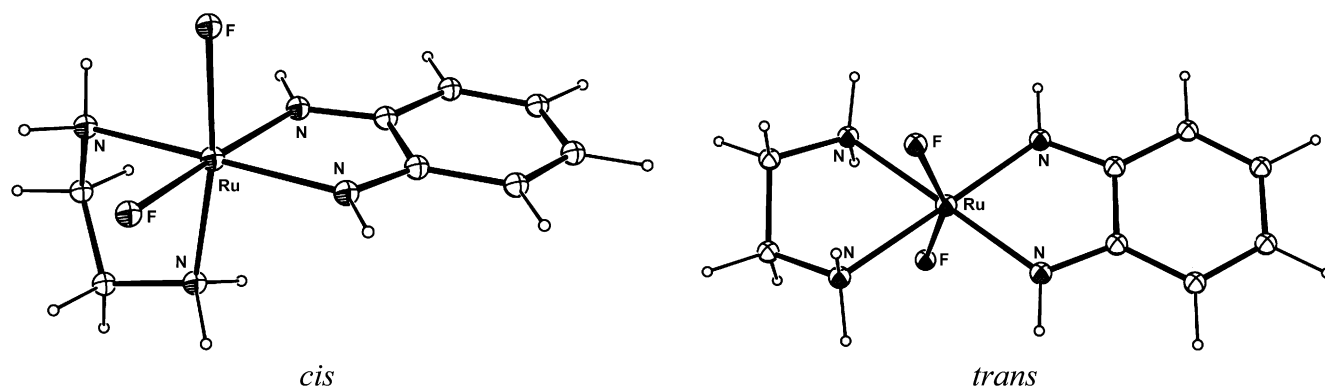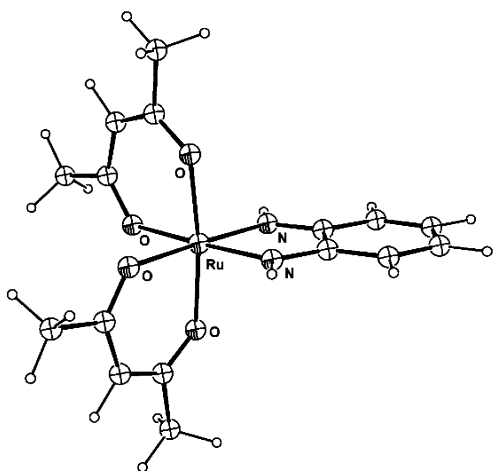**Figure 4.** Molecular diagrams of *cis*- and *trans*-$[Ru(bqdi)(en)F_2]$ complexes.

Figure 5. Molecular diagram of the $[Ru(bqdi)(acac)_2]$ complex.

ethylendiamine (en) ligands (Table 2). For the *cis*-$[Ru(bqdi)-(en)F_2]$ complex (Figure 4) two NICS(1) parameters for the bqdi-chelate ring are displayed. The first one is determined at the side of the ring with axial fluoro ligand, and the second one, at the side with axial nitrogen atom; there is only a small difference between these two NICS(1) values. In all the Ru^{2+} complexes, the NICS values of the Ru^{2+}−bqdi chelate ring indicate aromaticity of the chelate ring; the NICS(1) values are in the range from −7.20 to −12.00 (Table 2). The values show that different ligands in the complexes have moderate influence on the aromaticity of the Ru^{2+}−bqdi chelate ring and cannot cause loss of aromaticity. The NICS(1) values are larger in the *cis*- and *trans*-$[Ru(bqdi)(en)F_2]$ (Figure 4) than in $[Ru(bqdi)_2F_2]$ and $[Ru(bqdi)_2(acac)_2]$ (Figure 5) complexes indicating that presence of other chelate rings with a delocalized π-system

causes the reduction of the NICS value of the Ru^{2+}−bqdi chelate ring.

The results presented for the Ru^{2+}−bqdi chelate ring support the previous findings about aromaticity of this chelate ring.[2,37] The calculated NICS values for the Ru^{2+}−bqdi chelate ring are in agreement with the experimental magnetic properties. The experimental data for the ^{1}H NMR spectra of the $[Ru(bqdi)(bpy)_2]^{2+}$ and $[Ru(NH_3)_4(bqdi)]^{2+}$ complexes show magnetic anisotropy due to matallacycle aromaticity in these complexes.[2,37] In addition, other experimental findings support aromaticity in the Ru^{2+}−bqdi chelate rings. The spectra of the complexes with the Ru^{2+}−bqdi chelate rings have an intense band in the visible region assigned to a π(metal + ligand) → π*(metal + ligand) transition.[2] The $Ru(3d_{5/2})$ binding energy of the complex[2] obtained from the X-photoelectron spectroscopy experiment lies in between the values for the Ru(II) and Ru(III) reference compounds. This ambiguity in the metal oxidation state indicates that the ligand π orbitals become extensively involved in binding in this metalloaromatic chelate. The C−N stretching of the Ru^{2+}−bqdi chelate ring was assigned to a strong band in the 1330−1420 cm^{-1} region, with frequency reflecting the existence of bond between single and double.[2] Previous theoretical results[37] indicate very extensive mixing between the metal dπ and ligand π and π* orbitals, and consequently, these complexes are considered to be extensively delocalized.

We also calculated the NICS values for the Ru^{2+}−acac chelated ring in the $[Ru(bqdi)(acac)_2]$ complex. Although Ru^{2+} can maybe form an aromatic ring with the bqdi ligand,

(37) (a) Metcalfe, R. A.; Lever, A. B. P. *Inorg. Chem.* **1997**, *36*, 4762−4771. (b) Rusanova, J.; Rusanov, E.; Gorelsky, S. I.; Christendat, D.; Popescu, R.; Farah, A. A.; Beaulac, R.; Reber, C.; Lever, A. B. P. *Inorg. Chem.* **2006**, *45*, 6246−6262.

it cannot form an aromatic ring with the acac ligand. Judging from the NICS(1) values, the acac chelate ring is not aromatic (Table 2) as it was also the case with aforementioned acac complexes with Pt^{2+}, Ni^{2+}, Mg^{2+}, and Ca^{2+} (Table 1).

The data collected in Table 2 show that the aromaticity of some benzene rings is reduced and even lost upon complexation. The calculated NICS values for the benzene ring of the bqdi ligand show that the benzene ring retains its aromatic character when the chelate ring can be considered as aromatic. On the other hand, positive NICS values for the benzene ring are obtained in cases when the chelate ring is not aromatic. These results suggest that the aromaticity of chelate and benzene rings in coordinated bqdi ligand are correlated. We also analyzed the corresponding HOMA (harmonic oscillator model of aromaticity)[38] indices for the benzene rings in complexes from Table 2 and find out that HOMA and NICS(1) values for benzene rings are correlated as is shown in Figure 6.

Conclusion

Calculations of NICS values on number of complexes with acetylacetonato (acac) and *o*-benzoquinonediimine (bqdi) ligands coordinated to different metals show that most of these chelate rings do not have large negative NICS values, indicating that these chelate rings do not satisfy this magnetic criterion for aromaticity. Among calculated chelate rings, there is only the Ru^{2+}−bqdi chelate ring with large negative NICS values, indicating aromaticity by magnetic criterion. The results shows that the chelate rings of bqdi ligand with other metals (Ni^{2+}, Pt^{2+} Os^{2+}, Rh^{3+}, Ir^{3+}) do not have large negative NICS values. These results demonstrate possibility that aromatic chelate rings can be formed only when certain metal and ligand are interacting. We found large negative
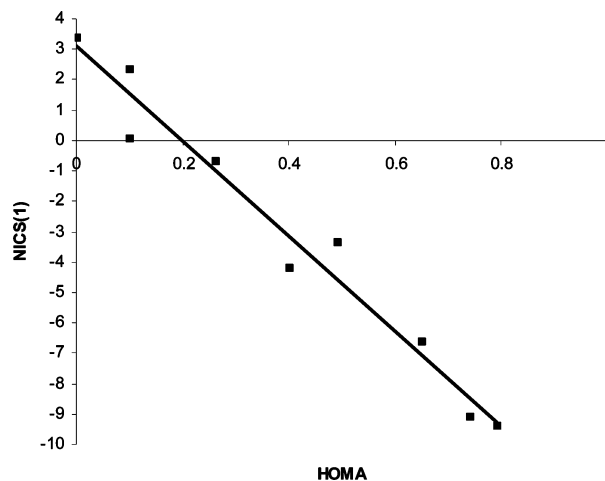
(38) (a) Krygowski, T. M. *J. Chem. Inf. Comput. Sci.* **1993**, *33*, 70−78. (b) Krygowski, T. M.; Cyranski, M. *Tetrahedron* **1996**, *52*, 1713−1722. (c) Krygowski, T. M.; Cyranski, M. *Tetrahedron* **1996**, *52*, 10255−10264.

Figure 6. Correlation between the NICS(1) and HOMA values of the benzene rings in the complexes presented in Table 2 (correlation coefficient $R^2 = 0.9652$).

NICS values for Ru^{2+}−bqdi chelate rings in number of complexes, with a variety of other ligands, indicating that other ligands in complexes have moderate influence on the delocalization in the Ru^{2+}−bqdi chelate ring.

Both acac and bqdi chelate rings can make noncovalent interactions in the way similar to that for the benzene ring; acac can make CH/π interactions, while the bqdi chelate ring can make CH/π and stacking interactions. The results presented here also demonstrate that one cannot make a conclusion about the aromaticity of the chelate ring on the basis of the noncovalent interactions that the chelate ring forms.