Intramolecular Metal Ligand Aromatic Cation−π Interactions in Crystal Structures of Transition Metal Complexes

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Dedicated to Prof. M. B. Ćelap on the occasion of his 80th birthday

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Cation–π interactions between ligands coordinated to a metal cation and aromatic groups have been predicted by theoretical calculations, and have been found in crystal structures of metalloproteins from the Protein Data Bank (PDB). We proposed metal ligand aromatic cation–π (MLACπ) interaction as intramolecular interactions in transition metal complexes. Searching crystal structures of transition metal complexes from the Cambridge Structural Database (CSD) reveals that there are quite a number of metal complexes, where an aromatic ring interacts with a hydrogen atom from a ligand in the same complex. The hydrogen atom is separated from the metal center by a few bonds and gains positive charge from the metal atom. In the complexes there are various metal atoms and various ligands. In the most of the complexes, the aromatic ring is separated from the metal center by two or four bonds, and interacts with the hydrogen atom of another ligand. In complexes where the aromatic ring is separated from the metal center by four or five bonds, there are examples of aromatic groups interacting with the hydrogen atom in the same ligand. By quantum chemical computations it was evaluated for the model systems of cationic cobalt(III) complexes with a charge of +1, that the energy of this intramolecular MLACπ interaction is about 4 kcal/mol.

Introduction

The cation−π interaction is considered an important non-covalent bonding force in a wide range of molecular systems.[1,2] Gas-phase studies of ion-molecule complexes established that cations bind strongly to molecules with π bonds.[2] High-level theoretical studies of ion−molecule systems have shown excellent agreement between calculated and experimental bonding energies, and have shown the geometries of the ion−molecule complexes.[3−15] The experimental and theoretical studies provide an understanding of the nature of the cation−π interaction.[1,16−18]

Cation−π interactions are important for molecular recognition in many biological systems.[1,2] Investigations on cation−π interactions in proteins show that cation−π interaction pairs contribute at least as much to protein stability and the structural motifs of a native protein as more conventional interactions. Hence, it was proposed that cation−π interactions should be considered the same way as hydrogen bonds, salt bridges, and hydrophobic effects in analyses of the stability of the native protein structure.[16,19,20]

Recently, the interaction of metal complexes as cations with π systems were investigated.[21−23] It is possible to predict cation−π interactions by quantum chemical calculations, since in theoretical work it was shown that calculated interaction energies for cation−π systems are in agreement with experimental data.[3−15] In our previous work, the interactions of π systems with the cationic metal complex $[Co(NH_3)_6]^{3+}$ were predicted by quantum chemical calculations. The bonding energies obtained with the B3LYP method for benzene, acetylene, and ethylene π complexes are 31.34 kcal/mol,[21] 18.30 kcal/mol, and 17.02 kcal/mol,[22] respectively. Since these calculations showed strong cation−π interactions, we proposed[21,22] that the cation−π interaction may exist when ligands coordinated to a metal ion can get in contact with π systems. This can be the case in metalloproteins, in metal complexes, in supramolecular structures, and when DNA and RNA interact with metal cations.

Cation−π interactions with a cationic metal complex were observed by analyzing crystal structures of DNA and RNA. It was noticed that cation−π interactions of divalent cations with the π systems of bases are important in stabilizing unstacked conformations of DNA and RNA.[24,25] Metal ligand aromatic cation−π (MLACπ) interactions in metalloproteins were discovered by searching crystal structures of metalloproteins from the Protein Data Bank (PDB).[23] These data reveal that there are quite a number of metalloproteins, where aromatic rings from phenylalanine, tyrosine, and tryptophan are close to a metal center, interacting with coordinated ligands. Among these ligands are amino acids like asparagine, aspartate, glutamate, histidine, and threonine, but also substrates like water and ethanol. These interactions play a role in stability and conformation of metalloproteins, and in some cases may also be directly involved in the mechanism of enzymatic reactions which occur at the metal center. For the enzyme superoxide dismutase, we evaluated by quantum chemical

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computations that Trp163 has an interaction energy of 10.09 kcal/mol with the ligands coordinated to the iron center.

We propose that intraligand MLACπ interactions, where ligands coordinated to a metal center interact with aromatic groups, exist in transition metal complexes. Intermolecular interactions between hydrogen atoms and π systems have been noticed in organometallic crystals.[24] In this work, we screened crystal structures of metal complexes in the Cambridge Structural Database (CSD) in order to find such intramolecular interactions. The structures with these interactions are described and the energy of the interactions was evaluated by quantum chemical calculations on model systems.

Results and Discussion

We have found that intramolecular MLACπ interactions, between a coordinated ligand and the aromatic ring in the

Table 1. Intramolecular metal-ligand cation−aromatic π interactions in complexes with two bonds between aromatic ring and metal center

#	Ref.	RFCODE[a]	*R* factor	Metal	X[b]	X···center of ring[c]	H···center of ring[d]	X···C[e]	H···C[f]	Y[g]
1	[27]	BZSACS	0.038	Co^{3+}	N	3.98	3.82	3.27	3.16	S
							3.35		2.83	
2	[28]	CUBXAY	0.051	Co^{3+}	N	3.39	3.54	3.22	3.00	P
							3.64		2.94	
					N	4.11	3.49	3.37	3.44	P
							4.17		2.89	
3	[29]	JORJAB	0.054	Co^{2+}	N	3.35	3.17	3.02	2.72	N
4	[30]	JUJPEJ	0.051	Cu^{2+}	N	3.92	3.22	3.36	2.82	N
5	[31]	TSACOP	0.039	Co^{3+}	N	3.79	3.45	3.12	2.96	S
							3.39		2.80	
6	[32]	TULBEH	0.051	Mn^{1+}	N	3.77	2.95	3.19	2.51	P
7	[33]	GAFKED10	0.028	Cd^{2+}	N	3.65	2.81	3.33	2.52	N
8	[34]	HELYUS	0.036	Ru^{2+}	N	3.83	3.06	3.18	2.61	S
9	[35]	PAXCAS	0.049	Mo^{4+}	N	3.89	3.13	3.07	2.43	S
10	[36]	PIRKAC	0.031	Ru^{1+}	N	3.55	3.39	3.14	2.92	P
							3.29		3.02	
11	[37]	TOJCIE	0.056	$Ru^{1/5+}$	O	3.94	3.00	3.27	2.37	P
12	[38]	VERGEE	0.048	Tc^{5+}	N	3.73	2.80	3.08	2.30	S
					N	3.72	2.80	3.04	2.25	S
13	[39]	WEFLOI	0.045	Ru^{2+}	N	4.02	3.36	3.28	2.71	Si
14	[40]	AQTPRU	0.048	Ru^{2+}	O	3.58		3.03		P
					O	2.74		3.09		P
15	[41]	KAJROC	0.027	Rh^{2+}	N	4.48	3.59	3.46	2.67	Sb
					N	4.15	3.26	3.36	2.63	Sb
16	[42]	BAXJOZ	0.034	Re^{4+}	O	3.98		3.34		P
17	[43]	CIRNUM	0.041	$Os^{2/3+}$	O	3.73		3.23		P
18	[44]	DIKMUF	0.058	Os^{2+}	O	3.64		3.14		P
					O	3.64		3.14		P
19	[45]	PEDXAX	0.056	Ir^{3+}	N	3.63	2.76	3.01	2.25	P
					N	3.71	3.05	3.09	2.64	P
							3.64		2.82	
20	[46]	PEWRUE	0.026	Re^{5+}	N	3.75		3.17		P
21	[47]	WAXGIL	0.055	Re^{3+}	N	3.53	2.69	3.14	2.48	P

[a] BZSACS, pentaammine(benzenesulfonyl)cobalt(III); CUBXAY, *cis*-(*NCS*,*NCS*),*trans*-(*P*,*P*)-bis[(2-aminoethyl)diphenylphosphanyl-*N*,*P*]di(isothiocyanato)cobalt(III); JORJAB, aniline(chloro)bis(ethylendiamine)cobalt(II); JUJPEJ, *catena*-[diamminobis{2-(*p*-aminobenzensulfonamido)-5-ethyl-1,3,4-thiadiazole-*N*,*N''*}copper(II)]; TSACOP, pentaammine(*p*-toluenesulfonyl)cobalt(III); TULBEH, tricarbonyl(hydrazine)bis(phenyl diethylphosphonite)manganese(I); GAFKED10, *catena*-[bis(μ-cyano-*C*,*N*)dicyano(μ-1,6-diaminohexane-*N*,*N*)bis(*p*-toluidine-*N*)−cadmium(II)−nickel(II)]; HELYUS, [1,2-bis(2-aminophenylthio)phenylene]dichloro(triphenylphosphane)ruthenium(II); PAXCAS, (diphenylmethylphosphane)hydrido(phenylhydrazine)tris(2,4,6-triisopropylphenylthiolato)molybdenum(IV); PIRKAC, *trans*(Ammino-bis(1,2-bis(diphenyl-phosphanyl)ethane)-phenylethynyl)-ruthenium(I); TOJCIE, dodecacarbonyl[μ_5-2-(diphenylphosphanyl)ethynylidene][μ-bis(diphenylphosphanyl)methane][1-(2-diphenylphosphanylphenyl)ethyl](μ-hydroxo)pentaruthenium; VERGEE, nitridobis(2,3,5,6-tetramethylbenzenethiolato-*S*)bis(1,1,2,2-tetramethylguanidine-*N*)technetium(V); WEFLOI, bis(benzylamino)dicarbonyl(phenyldimethylsilyl)(iodo)ruthenium(II); AQTPRU, aquadicarbonyl(hydrido)bis(triphenylphosphane)ruthenium(II); KAJROC, tris(μ-acetamidato-*N*,*O*)(μ-acetato-*O*,*O'*)bis(triphenylstibine)dirhodium(II); BAXJOZ, *trans*-trichlorobis(diethylphenylphosphane)(hydroxo)rhenium(IV); CIRNUM, 1,1,2,2,2,3,3,3,3-nonacarbonyl-1-(dimethylphenylphosphane)-1,2-(μ-hydrido)-1,2-(μ-hydroxo)triosmium; DIKMUF, (aqua)dicarbonyl(hydrido)bis(triphenylphosphane)osmium(II); PEDXAX, *trans*,*mer*-[dichlorotris(dimethylphenylphosphanyl)amino]iridium(III); PEWRUE, chloro[*N*-(*N*,*N*-diethylthiocarbamoyl)benzamidinato]bis(dimethyl- phenylphosphane)(nitrido)rhenium(V); WAXGIL, ammine(benzoyldiazenido-*N*)dichlorobis(triphenylphosphane)rhenium(III). − [b] Heavy atom to which the interacting hydrogen atom is bound. − [c] The distance [Å] between the heavy atom and the center of the aromatic ring. − [d] The distance [Å] between the interacting hydrogen and the center of the aromatic ring. − [e] The distance [Å] between the heavy atom and the closest carbon atom of the aromatic ring. − [f] The distance [Å] between the interacting hydrogen atom and the closest carbon atom of the aromatic ring. − [g] he atom between the metal atom and the aromatic ring.

same complex, can be observed in a number of crystal structures of transition metal complexes. Data about these interactions in different crystal structures are compiled in Table 1 and Table 2. The data show that there are numerous metal complexes where there is close contact between an aromatic ring and a hydrogen atom from a ligand, and that different metal ions and ligands can be involved.

In all of the observed cases where this interaction occurs, the ligand interacting with an aromatic group possesses a hydrogen atom pointing towards the aromatic ring. A partial positive charge of the ligand, induced by the metal charge, is situated on the hydrogen atom interacting with the aromatic ring. In most of the crystal structures the positions of hydrogen atoms were given, and in Table 1 and Table 2 the distances from the interacting hydrogen atom to the center of the aromatic ring and to the closest carbon atom of the aromatic ring are given. We also list the distances from the heavy atom (oxygen or nitrogen) to which the hydrogen atom is bound.

Based on the type of the ligand containing with the aromatic group, we can separate the metal complexes with MLACπ interactions into two groups. In the first group are

Table 2. Intramolecular metal-ligand cation−aromatic π interactions in complexes with several bonds between aromatic ring and metal center

#	Ref.	RFCODE[a]	R factor	Metal	X[b]	X···center of ring[c]	H···center of ring[d]	X···C[e]	H···C[f]
1	[48]	CEBREG	0.052	Cu^{2+}	N	4.00	3.42	3.06	2.66
2	[49]	FUCSIF	0.029	Cu^{2+}	N	3.90	3.29	2.96	2.58
3	[50]	NEFRAR	0.050	Co^{3+}	N	3.90	3.22	2.99	2.54
4	[51]	POKMAD02	0.041	Co^{3+}	N	3.75	3.08	2.90	2.56
					N	3.75	3.08	2.90	2.56
5	[52]	TONPUH	0.04	Cu^{2+}	N	3.88	2.99	2.99	2.23
6	[53]	VAFSIE	0.054	Co^{3+}	N	3.85	3.03	2.92	2.33
7	[54]	RUFKUY	0.019	Rh^{3+}	N			2.93	2.46
8	[55]	NEGREW	0.023	Re^{1+}	N	3.81	3.16	2.82	2.38
						3.55	2.87	3.29	2.51
9	[56]	DUSJIK	0.044	Ni^{3+}	N	3.27	2.21	3.46	2.54
10	[57]	DEMHAE	0.056	Ni^{2+}	N	3.55	2.87	3.29	2.62
						3.55	2.87	3.29	2.51
11	[58]	DIXHAT	0.051	Cu^{2+}	N	4.48	3.79	3.84	3.18
					N	4.53	3.84	3.84	3.18
12	[59]	GLTRCU01	0.041	Cu^{2+}	O	3.25	2.31	3.37	2.52
13	[60]	LETYCU10	0.035	Cu^{2+}	O	3.32	2.58	3.39	2.66
14	[61]	NALPIZ	0.057	Fe^{2+}	N	3.63	2.63	3.16	2.72
					N	3.63	2.63	3.16	2.29
15	[62]	NOVBAB	0.060	Ni^{2+}	O	4.06	3.28	3.53	2.76
					O	3.93	3.23	3.27	2.49
16	[63]	NUTKES	0.048	Mn^{2+}	O	3.24	2.36	3.32	2.74
					O	4.13	3.22	3.52	2.65
17	[52]	TONPOB	0.034	Cu^{2+}	O	3.17		3.31	
18	[64]	FOBTAR	0.038	Mo^{4+}	N	3.42	2.84	3.26	2.53
19	[65]	SIRCOL	0.047	Mo^{4+}	N	3.91	2.97	3.50	2.67
					N	3.91	2.97	3.50	2.67
20	[66]	ZURREJ	0.042	Cd^{2+}, Ni^{2+}	N	3.77	2.91	3.55	2.68
21	[67]	NOLQIO	0.031	Mo^{6+}	N	3.47	2.94	3.33	2.85

[a] CEBREG, (dimethyl sulfoxide)bis(L-phenylalaninato)copper(II); FUCSIF, [(*R*)-2-amino-1,1-bis(2-methoxyphenyl)-3-phenylpropanol-*N*,O])-[(*R*)-1,1-bis(2-methoxyphenyl)-3-phenyl-2-saliciylideneamino-1-propanolato-*N*,*O*,*O′*]copper(II); NEFRAR, Δ-α-[*N*,*N′*-dimethyl-*N*,*N′*-di(2-picolyl)-1*S*,2*S*-diaminocyclohexane](*S*-phenylalaninato)cobalt(III); POKMAD02, hydrogen[bis{*N*-(3-hydroxy-5-hydroxymethyl-2-methylpyridin-4-ylmethyl)-L-phenylalaninato}]cobalt(III); TONPUH, *catena*-[(μ_3-L-leucyl-L-phenylalaninato)copper(II)]; VAFSIE, (−)-Λ-β_2-[*N*,*N′*-{bis(1,1,1-trifluoro-4-imino-2-pentanonato)ethylene-*O*,*O′*,*N*,*N′*}(l-phenylalaninato-*O*,*N*)cobalt(III)]; RUFKUY, chloro[hydrotris(3,5-dimethylpyrazolyl)borato](L-tryptophanato)rhodium(III); NEGREW, octacarbonyl(μ-benzophenone hydrazinato)(μ-hydrido)dirhenium(I); DUSJIK, aqua(15-benzyl-1,13-didehydro-1,4,7,10,13-pentaazacyclohexadecane-14,16-dione-*N*,*N′*,*N′′*,*N′′′*,*N′′′′*)-nickel(III); DEMHAE, [{*cis*-bis(isothiocyanato-*N*)}bis{(*R*)-(+)-1-phenyl-1-ethylamine-*N*}bis{(*S*)-(−)-1-phenyl-1-ethylamine-*N*}-nickel(II){*cis*-bis(isothiocyanato-*N*}tetrakis{(*R*)-(+)-1-phenyl-1-ethylamine-*N*}nickel(II)]; DIXHAT, bis(μ-2-amino-2-methyl-1-propanolato-*O*,*O*,*N*)bis(2-amino-2-methyl-1-propanol-*N*,*O*)tetrakis(phenylacatato-*O*)tricopper(II); GLTRCU01, diaqua(glycyl-L-tyrosyl)-copper(II); LETYCU10, *catena*-[aqua(μ-L-leucyl-L-tyrosinato)copper(II)]; NALPIZ, amminebis[diphenylborato(dimethylglyoximato)]-pyridineiron(II); NOVBAB, (*R*,*R*)-triaqua-4,6-dibenzofurandiyl-2,2′-bis(4-phenyloxazoline)nickel(II); NUTKES, *catena*-[tetraaquabis(μ-triphenylacetato)bis(triphenylacetato)dimanganese(II)]; TONPOB, *catena*-[aqua(μ-L-leucil-D-phenylalaninato)copper(II)]; FOBTAR, (2,6-diphenylphenoxy-*O*)bis(2,6-diphenylphenoxy-*O*)(dimethylammonio)molybdenum(IV); SIRCOL, *trans*-bis(dimethylamine-*N*)tetrakis(2-phenylphenoxy-*O*)molybdenum(IV); ZURREJ, *catena*-[bis(μ-cyano)bis(μ-*p*-xylylenediamine)dicyanocadmium(II)nickel(II)]; NOLQIO, triethylammonium [*mer*-trichloro(diphenylmethylimido)(2,2-diphenylglycinato)molybdenum(VI)]. − [b] Heavy atom to which the interacting hydrogen atom is bound. − [c] The distance [Å] between the heavy atom and the center of the aromatic ring. − [d] The distance [Å] between the interacting hydrogen and the center of the aromatic ring. − [e] The distance [Å] between the heavy atom and the closest carbon atom of the aromatic ring. − [f] The distance [Å] between the interacting hydrogen atom and the closest carbon atom of the aromatic ring.

complexes where the aromatic group is bound to the atom that is coordinated to the metal ion. In this way there are only two bonds between the metal center and the aromatic group (Figure 1, a and b). In the second group are complexes where the aromatic group is separated from the metal center by several bonds (Figure 1, c, d, and e).

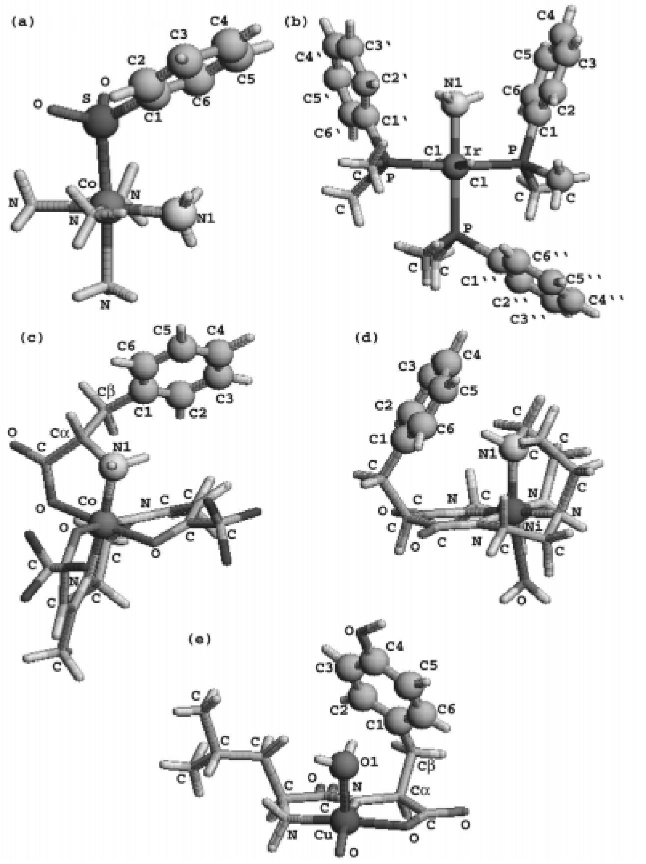

Figure 1. Structures of complexes with intramolecular MLACπ interaction; (a) BZSACS, (b) PEDXAX, (c) VAFSIE, (d) DUSJIK, (e) LETYCU10

Complexes with Two Bonds between the Aromatic Ring and the Metal Center

In these complexes, organic ligands with aromatic groups can make MLACπ interactions only if the ligand is coordinated in a *cis* position, and there is no possibility for such an interaction within the same ligand. In the structures given in Table 1 the aromatic ring is bonded to the atoms N, P, S, Si, Sb (last column in Table 1), while at the same time these atoms are coordinated to the metal ion. The carbon atom of the aromatic ring that is the closest to the interacting hydrogen atom is the one that is bonded to the heteroatom, and is the closest to the metal center (C1 in Figure 1, a). An example for this type of complex, structure BZSACS, is shown in Figure 1, a. In this complex, a cobalt ion is octahedrally coordinated by five NH_3 groups and the sulfur atom of a benzenesulfinato ligand. The phenyl ring of the benzenesulfinato ligand interacts with the hydrogen atoms of the NH_3 ligand in *cis* position. In the crystal structure there are two hydrogen atoms oriented towards the aromatic ring, with the distances to the closest carbon atom of 3.16 and 2.83 Å. The torsion angle C1−S−Co−N1 is 15.8° which is very favorable for a MLACπ interaction.

In other complexes (structures CUBXAY, TSACOP, PIRKAC, PEDXAX) there are also two hydrogen atoms of the same ligand interacting with the same aromatic ring (Table 1). In some complexes there are two MLACπ interactions in the same complex. In the structures AQTPRU, DIKMUF, PEDXAX, and WAXGIL there are two aromatic groups of two ligands interacting with the hydrogen atoms of the same ligand (Table 1). The structure of the *trans,mer*-$[IrCl_2(NH_3)(PMe_2Ph)_3]^+$ complex (PEDXAX) is shown in the Figure 1, b. Two PMe_2Ph ligands, which are in *cis* positions relative to the NH_3, have phenyl groups oriented towards NH_3. The torsion angles C1−P−Ir−N1 and C1′−P−Ir−N1 are 7.5 and 26.9°, and the N1−C1 and N1−C1′ distances are 3.01 and 3.09 Å, respectively (Table 1, column 7). In this structure there is one more MLACπ interaction, that is not listed in the Table 1, since we searched and listed only interactions where there are two bonds between the hydrogen atom and the metal center. The third interaction in this complex is the interaction of a third phenyl group with the hydrogen atom of the CH_3 group (Figure 1, b); the C1′′−H distance is 2.43 Å.

It can be expected that when the interacting hydrogen atom is separated from the metal center by more bonds it could gain less positive charge from the metal ion, resulting in a diminished interaction. However, here we are considering intramolecular interactions, and there are many steric constrains. Hence, it is not possible to observe a regular correlation between the interaction distances and the amount of positive charge on the hydrogen atom, as is possible with metalloproteins where MLACπ interactions are not as constrained by steric influences.[23] It is interesting to point out that from spectra of the *trans,mer*-$[IrCl_2(NH_3)(PMe_2Ph)_3]^+$ complex in solution, it is evident that there is rapid rotation about the Ir−P bonds,[45] which means that there are no MLACπ interactions in solution.

The structures TOJCIE, KAJROC, and CIRNUM are structures of binuclear complexes. In these three complexes the aromatic rings interact with the hydrogen atoms of the ligands in the bridge.

In the complexes listed in the Table 1 there is not much freedom for the ligands to adjust their mutual orientation. Due to steric constraints, the mutual orientation of the aromatic ring and the interacting hydrogen atom of the ligand in a *cis* position is such that the hydrogen atom and the heavy atom are close to the C1 atom of the aromatic ring, but rather far from its center (Figure 1, a). This can also be noticed by comparing the interaction distances in these complexes (Table 1) with the distances in other complexes listed in Table 2.

Complexes with Several Bonds between the Aromatic Ring and the Metal Center

The data for these complexes are shown in Table 2. In most of the structures there are four bonds between the metal center and the aromatic ring, but there are a few exceptions. In the structures DEMHAE, NOVBAB, ZURREJ, and NOLQIO, there are three bonds between the metal center and the aromatic ring, and in structure DUSJIK there are five bonds.

In the structures with several bonds between the metal center and the aromatic ring there is a possibility for MLACπ interactions with the hydrogen atom of another ligand, but also with the hydrogen atom of the same ligand (structures 1−8 in Table 2). In the phenylalaninato complex (structure VAFSIE, Figure 1, c) there is an intraligand MLACπ interaction, where the phenyl ring interacts with the hydrogen atom bonded to the coordinated nitrogen atom. The value of the torsion angle C1−Cβ−Cα−N1 is −52.8°. Due to steric constraints, as in all other structures with intraligand MLACπ interactions, the closest carbon atom to the interacting hydrogen atom is C1 (Figure 1, c). The C1−H distance is 2.33 Å, one of the shortest C−H distances among complexes listed in Table 2. In the structure NEGREV there is a binuclear complex, and the ligand with intraligand MLACπ interaction is in the bridge, coordinated to both metal ions.

For complexes with an intraligand MLACπ interaction, the range of the interaction distances (Table 2, structures 1−8) is small compared to other complexes with such interactions (Table 1 and Table 2). For example, the C−H distances range from 2.66 to 2.23 Å, which is smaller than in other complexes in Table 1 and Table 2 (structures 10−22). The C−H and C−N distances are the shortest (Table 1 and Table 2), but distances to the center of the aromatic ring are longer than for other complexes in Table 2. The reason for the small range of distances is that in all these complexes the interactions are very similar, and in all cases there are very strong steric constraints as the aromatic group and the interacting hydrogen atom are on the same ligand. At the same time the steric constrains do not allow the hydrogen atom to be directed to the center of the ring, but it remains close to only one or two carbon atoms in the ring.

Among all structures in Table 1 and Table 2, DUSJIK is the structure with the shortest distance between the hydrogen atom and the center of the ring. It is a very special structure, where Ni^{III} is coordinated by one pentadentate ligand and a water molecule. A pentadentate ligand is coordinated with five nitrogen atoms and has a benzyl group (Figure 1, d). There are a large number of bonds between the aromatic ring and the interacting hydrogen atom, and there is a possibility for the phenyl ring to orient itself in a way that the interacting hydrogen atom is directed to the center of the aromatic ring. The distance from the hydrogen atom to the center of the ring is 2.21 Å. The authors[56] noticed an unusual orientation of the benzyl group and a very short distance between the hydrogen atom and the aromatic ring, and attributed this to π-electron donor−acceptor interactions.

Among the structures where the aromatic group is separated from the metal center by several bonds (Table 2) there are a number of structures where the aromatic ring interacts with the hydrogen atom of another ligand (structures 10−22). In the structure LETYCU10 there is a five-coordinate complex of Cu^{II} (Figure 1, e). The dipeptide L-leucyl-L-tyrosine is coordinated as a tridentate chelate; the fourth coordination site is occupied by water. The fifth ligand is the carboxyl oxygen atom of a dipeptide, coordinated to another metal atom. In this way there are chains in the crystal structure. The aromatic ring interacts with the hydrogen atom of coordinated water. In this structure the interacting hydrogen atom is closer to the center of the ring (2.58 Å) than to the carbon atom (2.66 Å) (Table 2).

The ligand with the interacting hydrogen atom is very often coordinated water (all examples in Table 2, where the heavy atom is oxygen). In other cases the interacting hydrogen atom is part of some coordinated amine. In structures NALPIZ and ZURREJ there is a simple NH_3 ligand.

In many of the structures there are two MLACπ interactions in the same complex. In some complexes there are two pairs of identical ligands making almost identical interactions, as in the structures DEMHAE, DIXHAT, and NOVBAB (Table 2). In case of NALPIZ, two phenyl groups interact with the same NH_3 ligand, and it is the only structure in this group with this type of interaction. In the structure NUTKES, the complex is binuclear. In this case, in one of the MLACπ interactions the aromatic group is of the ligand forming the bridge, in the other interaction an aromatic group of one metal ion interacts with the H_2O molecule ligated to the other metal ion. These two interactions are rather different (Table 2).

In the complexes with the aromatic ring separated from the metal center by several bonds and interacting with hydrogen atoms of another ligand (Table 2, structures 11−22) there are less steric constraints preventing the interaction of the whole aromatic ring. Here the interaction distances to the center of the ring are shorter, and at the same time the distances to the closest carbon atom are longer compared with other complexes (Table 1 and Table 2, structures 1−8).

Calculated Intramolecular MLACπ Interactions

Since the complexes in which intramolecular MLACπ interactions exist are rather large, for DFT calculations model systems with smaller ligands were used. The geometries and energies for structures with various conformations of the aromatic ring in the model systems were calculated. Based on the difference in energy for conformers with and without MLACπ interactions, the energy of the interactions was evaluated. It can be expected that the partial positive charge on interacting hydrogen atoms depends on the charge of the whole complex. By quantum chemical calculations it was shown that the MLACπ interaction is stronger if the complex is more positively charged.[68] The evaluated energy in these calculations is for the model systems of cationic complexes of Co^{III} with charge of +1.

Calculations on Complexes with Two Bonds between the Aromatic Ring and the Metal Center

A suitable model system for calculations on this type of interactions was the cobalt(III) complex $[CoCl_2(NH_3)_3$-

Table 3. Some geometrical data of optimized conformers of model systems

Structure[a]	Type of interaction	Torsion angle [°][b]	N···center of ring [Å]	H···center of ring [Å]	N···C [Å]	H···C [Å]
$[CoCl_2(NH_3)_3(C_6H_5NH_2)]^+$	ligand in *cis* position	2.6	3.638	2.721	2.965	2.269
$[CoCl(NH_3)_3Phe]^+$	intraligand	49.8	3.875	3.091	2.973	2.425, 2.497
	ligand in *cis* position	49.8	3.674	2.654	3.584	2.579
	intraligand	−50.8	3.859	3.112	2.964	2.439, 2.683

[a] Structures are shown in Figure 2. – [b] In case of $[CoCl_2(NH_3)_3(C_6H_5NH_2)]^+$, the torsion angle is C1−N1−Co−N2, in case of $[CoCl(NH_3)_3Phe]^+$ the torsion angle is C1−Cβ−Cα−N1.

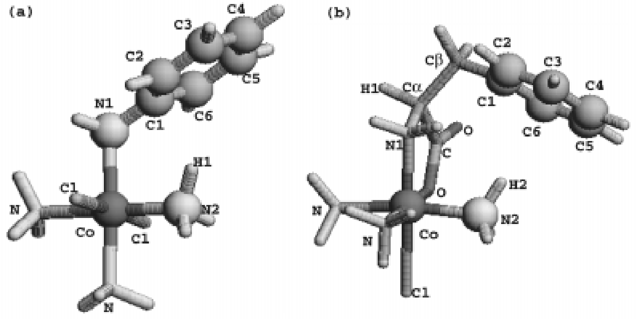

Figure 2. Geometries of model systems used for calculations of intramolecular MLACπ interactions: (a) $[CoCl_2\ (NH_3)_3(C_6H_5NH_2)]^+$, (b) $[CoCl\ (NH_3)_3Phe]^+$

$(C_6H_5NH_2)]^+$ (Figure 2, a). The coordinated aniline molecule has two NH_3 and two Cl^- ligands in *cis* positions. Optimizing the geometry for this complex always gives a structure where the aromatic ring is situated above the NH_3 group. In this structure the torsion angle C1−N1−Co−N2 (Figure 2, a) is 2.6°. One hydrogen atom of the NH_3 ligand is oriented towards the aromatic ring. The interaction distances C1···H1 and C1···N2 are 2.269 and 2.965 Å, respectively (Table 3). These distances are a little shorter than distances found in the crystal structures (Table 1). In order to find the energy of the geometry where the aromatic ring is above Cl we fixed the torsion angle C1−N1−Co−Cl to 2.6°, a value that we obtained for the torsion angle C1−N1−Co−N2 of the optimized structure. The difference in energy for structures where the aromatic ring is above the NH_3 and Cl^- ligands is 7.28 kcal/mol. In the first structure the aromatic ring has attractive interactions with the partially positively charged hydrogen atom (+0.36), in the second one it has repulsive interactions with the partially negatively charged chloro ligand (−0.22). Hence, the difference in energy is not only caused by attractive MLACπ interactions, but also by repulsive interactions. We evaluate that the energy of MLACπ interaction is about half of this difference, so it is between 3.5 and 4.0 kcal/mol.

Calculations on Complexes with Several Bonds between the Aromatic Ring and the Metal Center

In these complexes there is the possibility for the aromatic ring to interact with a hydrogen atom in the same ligand, or with the hydrogen atom in another ligand. To study both of these interactions we used the $[CoCl(NH_3)_3Phe]^+$ complex as model system (Figure 2, b). In the coordinated phenylalaninato ligand there are three possible conformations of the phenyl ring, which can be defined by the torsion angle C1−Cβ−Cα−N1 (Figure 2, b). The ideal values for this torsion angle are 60°, −60°, and 180°. Using these ideal torsion angles as a starting point for the optimization, gave optimized structures with angles of 49.8, −50.8, and −143.6°, respectively (Table 3). In the first conformer (with a torsion angle of 49.8°) there is an intraligand MLACπ interaction and a MLACπ interaction with the *cis*-NH_3 ligand. In the conformer with a torsion angle of −50.8° there is only an intraligand interaction, and in the conformer with the torsion angle of −143.6° there is no interaction. The calculated distances for intraligand MLACπ interactions (Table 3) are in the range of distances that are observed in crystal structures (Table 2, structures 1−8). In the case of the interaction of the phenyl ring with the NH_3 ligand in *cis* position, the calculated C−H distance (Table 3) is shorter than most of the C−H distances in crystal structures, while the calculated C−N distance is longer than most C−N distances in crystal structures (Table 2, structures 11−22).

The conformer with only one intraligand MLACπ interaction is more stable then the conformer without MLACπ interaction by 3.63 kcal/mol. The conformer with two MLACπ interactions is more stable by 7.61 kcal/mol. Since the distances of intraligand interactions are very similar in both conformers (Table 3), one can conclude that the energies are also similar. It means that in the conformer with the two MLACπ interactions, about 3.5 kcal/mol is stabilization for the intraligand interaction and the rest of about 4 kcal/mol is stabilization of interaction with the ligand in the *cis* position.

Conclusion

MLACπ interactions are proposed as intramolecular interactions in metal complexes. By coordination to a metal cation, ligands get positive charge, and can interact with an aromatic ring in the same complex. The Cambridge Structural Database was systematically searched to find intramolecular interactions between ligands coordinated to a metal center and aromatic rings. It turned out that this type of interaction is ubiquitous in metal complexes. Examples were found for various metal ions and ligands. In most of the complexes there are two or four bonds between the metal center and the aromatic ring. The aromatic ring of an organic ligand can interact with a hydrogen atom of another ligand, or, in complexes where there are four or five bonds between the metal center and the aromatic ring also with hydrogen atoms of the same ligand. In this latter case, the aromatic ring can also interact with hydrogen atoms of the same ligand. The steric constraints in the complexes have an important influence on the geometry and probably the strength of intramolecular MLACπ interactions.

DFT calculations on model systems of Co^{III} complexes with a total charge of +1 have been done in order to evaluate the energy of intramolecular MLACπ interactions. Geometries and energies have been calculated for conformers with different orientations of the phenyl ring. Calculated geometric parameters of the interactions were very similar to those found in the crystal structures of complexes. By comparing the energies of conformers both with and without MLACπ interactions, we determined that the energy of interactions in these model systems is about 4 kcal/mol.

Experimental Section

Data Screening and Computational Methods: Crystal structures of metal complexes containing a phenyl ring and transition metal ions with coordinated nitrogen or oxygen atoms were extracted from the CSD. The structures of these metal complexes were screened for intramolecular cation−π interactions between ligands coordinated to the metal ion and aromatic groups using geometric criteria. We used the same criterion for distance as proposed by McFail-Isom et al.[25] for screening crystal structures of DNA for cation−π interactions between a metal ion and an aromatic base of DNA, for searching for MLACπ interactions in metalloproteins.[23] However, we did not use any restrictive criteria for the angle of the normal of the aromatic ring plane with the distance vector between the center of the aromatic ring and the metal center. Since in this case we were investigating intramolecular interactions, the aromatic ring is part of a ligand and therefore the orientation of the aromatic ring can be different. This is not the case where the aromatic group was not part of a coordinated ligand. We searched for structures, where the distance between the metal ion and the center of the aromatic ring is less than $d_0 = 5.5$ Å. Screening the CSD with the described criterion provided a large number of structures, where an aromatic ring is close to a metal center. We considered only structures with R factors < 0.06, and chose a number of structures where it was clear that an intramolecular MLACπ interaction between coordinated ligand and aromatic ring exists. Since it was shown that the interaction is stronger if the hydrogen atom that is interacting with the aromatic group is closer to the metal center,[23] we considered only structures where there are only two bonds between the hydrogen atom and the metal ion. − The optimized geometries and energies for the model system of the complexes with the cation−π interaction were obtained using the density functional theory (DFT) with the Becke (B3) three-parameter exchange function,[69] and the Lee−Yang−Parr (LYP) correlation functional.[70] These B3LYP calculations were carried out with the Gaussian98 program.[71] For all atoms the LANL2DZ basis sets were chosen. Recently, reliable results with DFT methods were obtained for other cation−π systems.[17][72−75] On the other hand, DFT methods also give good results for all transition metal complexes including transition metal complexes of the first row,[76−88] hence in this work the DFT method was used. − The geometries of all conformers of the model systems were fully optimized. Only in one case where the conformer was not a stationary point did we constrain the torsion angle of the aromatic ring in order to keep it in a certain position.

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