Metal-Induced Tautomerization of *p*- to *o*-Quinone Compounds: Experimental Evidence from Cu^I and Re^I Complexes of Azophenine and DFT Studies

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Dedicated to Professor Hans Bock on the occasion of his 75th birthday

Abstract: Azophenine (7,8-diphenyl-2,5-bis(phenylamino)-*p*-quinonediimine, L^p) reacts with $[Cu(PPh_3)_4](BF_4)$ or $[Re(CO)_5Cl]$ to yield the $(Ph_3P)_2Cu^+$ or $[(OC)_3ClRe]$ complex of the tautomeric form 7,8-diphenyl-4,5-bis(phenylamino)-*o*-quinonediimine, L^o, as evident from structure determinations and from very intense metal-to-ligand charge transfer (MLCT) transitions in the visible region. Time-dependent DFT (TD-DFT) calculations on model complexes $[(N{\cap}N)Re(CO)_3Cl]$ confirm the spectroscopic results, showing considerably higher oscillator strengths of the MLCT transition for the *o*-quinonediimine complexes in comparison to compounds with $N{\cap}N = 1,4$-dialkyl-1,4-diazabutadiene. The complexes are additionally stabilized through hydrogen bonding between two now *ortho*-positioned NHPh substituents and one fluoride of the BF_4^- anion (Cu complex) or the chloride ligand (Re complex). DFT Calculations on the model ligands *p*-quinonediimine or 2,5-diamino-*p*-quinonediimine and their *ortho*-quinonoid forms with and without Li^+ or Cu^+ are presented to discuss the relevance for metal-dependent quinoproteins.

Keywords: copper · density functional calculations · quinones · rhenium · tautomerism

Introduction

Metal-dependent quinoproteins[1,2] are known with the quinonoid cofactors pyrroloquinolinequinone (PQQ),[3] topaquinone (TPQ)[4] or lysine tyrosylquinone (LTQ).[5] Depending on the substitution pattern, an *o*- (PQQ,TPQ) or *p*-quinone form (TPQ)[6] is favored, however, *o*/*p* tautomeric high-energy species can be conveniently formulated in all instances (Scheme 1). The favored tautomers either avoid the formation of imine instead of carbonyl functions (PQQ, LTQ) or exhibit the established preference[7] for the *p*- over the *o*-tautomer (TPQ).

Using the all-nitrogen compound azophenine L^p, a long established *p*-quinonoid compound[8] with a hardly explored ligand potential in coordination chemistry,[9,10] we have previously shown that coordination of phosphine-stabilized copper(I) can cause tautomerization to the chelating *o*-quinonoid tautomer L^o (Scheme 2), supported by interionic ring-forming hydrogen bonding between the newly *o*-positioned NHPh substituents with one fluorine atom of the BF_4^- counterion.[11]

Metal-induced tautomerization is a phenomenon that has been discussed especially in connection with Pt^{II}–nucleobase interaction where stabilization of the “wrong” tautomer could lead to mispairing in nucleic acids.[12] Furthermore, metal-induced proton migration in coordination compounds is an important feature of functional systems devised for the field of molecular electronics.[13]

In this report we describe that the metal-induced tautomerization of azophenine can also occur in non-ionic systems by example of a structurally and spectroscopically characterized organorhenium(I) complex. To explore this phenomenon in a more general manner we also present DFT calculations on the model ligands *p*-quinonediimine and 2,5-diamino-*p*-quinonediimine and their *ortho*-quinonoid forms. These calculations were performed with and without Li^+ or Cu^+ present to evaluate the function of

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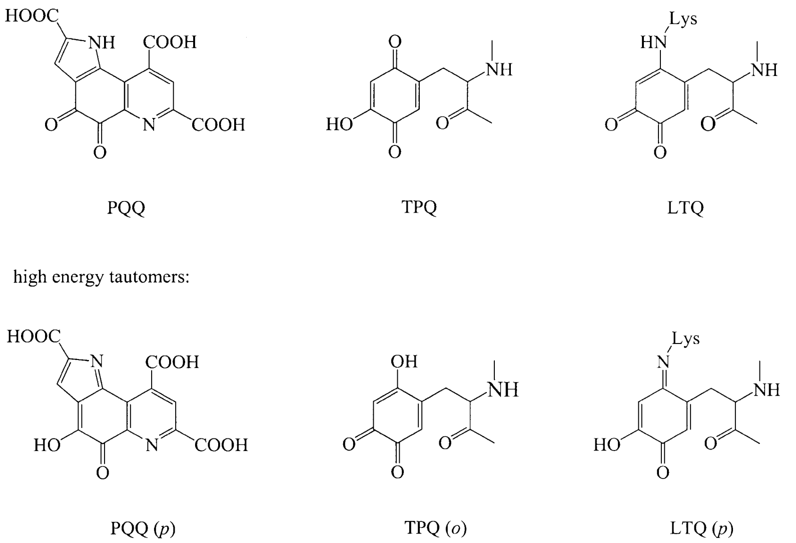


Scheme 1.

azophenine
(*p*-quinonoid tautomer L^p)

copper(I) complex
(*o*-quinonoid tautomer L^o as ligand)

Scheme 2.

metal coordination. Coordination compounds of *o*-quinones[14] and especially *o*-quinonediimines[14–16] have raised interest because of strong metal–ligand π interaction as evident from intense charge transfer bands, the potentially non-innocent behavior of the ligands,[14,15] and the capacity of intercalation into DNA.[16]

Experimental Section

Instrumentation: ^{1}H NMR spectra were taken on a Bruker AC 250 spectrometer, IR spectra were obtained using Perkin Elmer 684 and 1760X instruments. UV/Vis/NIR absorption spectra were recorded on Shimadzu UV160 and Bruins Instruments Omega 10 spectrophotometers. Cyclic voltammetry was carried out at 100 mV s^{-1} scan rate in 0.1 M Bu_4NPF_6 solutions using a three-electrode configuration (glassy carbon electrode, Pt counter electrode, Ag/AgCl reference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium couple served as internal reference.

Synthesis: The preparation of [(L^o)Cu(PPh$_3$)$_2$](BF$_4$) has been described previously.[11]

[(L^o)Re(CO)$_3$Cl]: [Re(CO)$_5$Cl] (140 mg, 0.39 mmol) and azophenine (180 mg, 0.41 mmol) were heated under reflux for 25 min in toluene (30 mL). The deep purple solution was evaporated to dryness. The solid was dissolved in a mixture of *n*-hexane and dichloromethane (3:1) and cooled to −25 °C. After 10 h a deep purple precipitate was collected, washed with *n*-hexane and dried under vacuum to yield the product (250 mg, 86 %). Elemental analysis calcd (%) for $C_{33}H_{24}ClN_4O_3Re$ (746.24): C 53.11, H 3.24, N 7.51; found: C 53.11, H 3.16, N 7.40; ^{1}H NMR (CD$_2$Cl$_2$): δ = 6.11 (s, 2H, H^{3,6}), 6.53 (br s, 2H, N-H), 7.05–7.46 (m, 20H, Ph); IR: $\tilde{\nu}_{NH}$ = 3288 cm^{-1} (KBr); $\tilde{\nu}_{CO}$ = 2015, 1927, 1898 cm^{-1} (CH$_2$Cl$_2$); UV/Vis (CH$_2$Cl$_2$): λ_{max} (ε) = 268(22 300), 289(sh), 389(12 600), 567(20 100), 625(sh).

Crystallography: Purple needles of [(L^o)Re(CO)$_3$Cl] were obtained through slow evaporation from an acetone solution layered with pentane. X-ray data were collected at 293(2) K on a four-circle diffractometer (Kappa-CCD, NONIUS) using graphite monochromated Mo$_{K\alpha}$ radiation (λ = 0.71073 Å). The structure was solved via direct methods using the programme SHELXS-97.[17a] Refinement was carried out by the full-matrix least-squares method employing the programme SHELXL-97:[17b] All non-hydrogen atoms were refined anisotropically. The C–H hydrogen atoms were introduced at appropriate positions with coupled isotropic factors using the riding model, the N–H hydrogen atoms were refined freely. Two crystallographically independent molecules were found in the unit cell. Absorption correction was performed numerically using the programme HABITUS.[18] Crystal data and selected structure parameters are listed in Tables 1 and 2.

CCDC-217 559 contains the suppplementary crystallographic data for this paper. These data can be obtaind free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

DFT Calculations: Ground state electronic structure calculations were done by density functional theory (DFT) methods using the Gaussian 98 program package.[19] The lowest excited states of the closed shell complexes were calculated by time-dependent DFT (TD-DFT). Double ζ basis sets 6-311G*[20] were employed for the H, C, N, O, Cl, Li and Cu

Table 1. Crystallographic data of (L^o)Re(CO)$_3$Cl.

empirical formula	$C_{33}H_{24}ClN_4O_3Re$
formula weight	746.24
crystal size [mm]	0.4 × 0.2 × 0.2
T [K]	293(2)
λ [Å]	0.71073
crystal system	orthorhombic
space group	$P2_12_12_1$ (No. 19)
a [Å]	9.4207(1)
b [Å]	20.3916(2)
c [Å]	34.1560(4)
cell volume [Å^3]	6561.47(12)
ρ_{calcd} [g cm^{-3}]	1.511
μ [mm^{-1}]	3.82
max. 2θ [°]	45.97
index ranges	$-10 \leq h \leq 10$ $-22 \leq k \leq 22$ $-37 \leq l \leq 37$
formula units per cell, Z	8
reflections collected	69 619
unique reflections	9115
R_{int}/R_σ	0.0798/0.0487
GOF/F^2	1.125
data/restraints/parameters	9115/0/770
Flack x parameter	0.00(1)
extinction	0.00033(5)
R indices (all data)	
R_1	0.0588
wR_2	0.0964
largest res. e$^-$ densities [e Å^{-3}]	0.95, −0.73

Table 2. Selected bond lengths and angles of [(L^o)Re(CO)$_3$Cl] (experimental) and [(Meap)Re(CO)$_3$Cl] (DFT calculated[a]).

Bond lengths [Å]	Exptl	Calcd	Bond lengths [Å]	Exptl	Calcd
Re1–C1	1.930(11)	1.932	N1–C4	1.342(11)	1.317
Re2–C51	1.910(14		N6–C56	1.293(12)	
Re1–C2	1.948(13)	1.932	N2–C5	1.290(11)	1.317
Re2–C52	1.895(14)		NS–C55	1.314(12)	
Re1–C3[b]	1.961(18)	1.962	C4–C5	1.507(13)	1.481
Re2–C53[b]	1.843(14)		C54–C55	1.482(14)	
Re1–N1	2.141(7)	2.155	C4–C9	1.403(13)	1.429
Re2–N6	2.153(9)		C54–C59	1.426(13)	
Re1–N2	2.161(7)	2.155	C5–C6	1.401(13)	1.429
Re2–N5	2.160(8)		C55–C56	1.400(13)	
Re1–Cl1	2.500(3)	2.522	C6–C7	1.381(13)	1.368
Re2–Cl2	2.508(3)		C56–C57	1.369(14)	
			C8–C9	1.337(13)	1.368
			C58–C59	1.345(14)	
			C7–N3	1.375(13)	1.389
			C57–N7	1.361(13)	
			C8–N4	1.353(14)	1.389
			C58–N8	1.380(13)	
			C7–C8	1.493(14)	1.465
			C57–C58	1.526(14)	

Bond angles [°]	Exptl	Calcd	Bond angles [°]	Exptl	Calcd
C1-Re1-C2	88.6(4)	91.4	C1-Re1-Cl1	92.8(4)	88.8
C51-Re2-C52	88.1(6)		C51-Re2-Cl2	95.4(4)	
C1-Re1-C3	89.1(5)	90.0	C2-Re1-Cl1	91.9(3)	88.8
C51-Re2-C53	88.2(5)		C52-Re2-Cl2	91.7(4)	
C2-Re1-C3	90.1(4)	90.9	C3-Re1-Cl1	177.3(3)	179.3
C52-Re2-C53	84.9(5)		C53-Re2-Cl2	175.0(4)	
C2-Re1-N1	97.9(4)	96.9	N1-Re1-Cl1	84.3(2)	84.9
C52-Re2-N6	102.6(4)		N6-Re2-Cl2	81.5(2)	
C1-Re1-N2	98.8(4)	96.9	N2-Re1-Cl1	83.2(2)	84.9
C51-Re2-N5	95.0(4)		N5-Re2-Cl2	85.1(2)	
C3-Re1-N1	93.5(3)	95.7	C4-N1-Re1	118.0(6)	116.6
C53-Re2-N6	95.6(4)		C54-N6-Re2	47.6(7)	
C3-Re1-N2	94.6(4)	95.7	C5-N2-Re1	117.3(6)	116.6
C53-Re2-N5	98.1(4)		C55-N5-Re2	117.1(7)	
N1-Re1-N2	74.6(3)	74.3	N1-C4-C5	112.8(8)	115.1
N6-Re2-N5	74.1(3)		N6-C54-C55	116.0(8)	
			N2-C5-C4	116.6(8)	115.1
			N5-C55-C54	114.9(9)	

[a] Symmetry averaged. [b] Bond to axial CO.

atoms, and quasirelativistic effective core pseudopotentials with a correspondingly optimized set of basis functions were used for Re.[21] Within TD-DFT calculations Dunning's polarized valence double ζ basis sets[22] were employed for the H, C, N, O and Cl atoms. In these calculations, the hybrid Becke's three parameter functional[23] with the Lee, Yang and Parr correlation functional (B3LYP) was used. The comparative TD-DFT calculations were performed using Becke's functional half-and-half exchange mixing[24] with LYP correlation (BHandHLYP).

Geometry optimization was performed for all systems and the vibrational frequencies were calculated for each stationary point. Energy minima were characterized either by the absence of imaginary frequencies or very low imaginary frequencies corresponding to the substituent rotation.

[(L^o)Re(CO)$_3$Cl] was modeled by the [(Meap)Re(CO)$_3$Cl] complex (Meap = 7,8-dimethyl-4,5-bis(methyl)-*o*-quinonediimine) in which the phenyl substituents on the nitrogen atoms of L^o were all replaced by methyl groups.

Results and Discussion

Formation of the complexes [(L^o)Cu(PPh$_3$)$_2$](BF$_4$) and [(L^o)Re(CO)$_3$Cl] occured in straightforward fashion from L^p and the precursors [Cu(PPh$_3$)$_4$](BF$_4$) or [Re(CO)$_5$Cl]. Dinuclear complex formation was not observed even in the presence of a 1:2 ligand-to-metal ratio. Whereas NMR and absorption spectra suggest only indirectly the formation of the above complexes with tautomerized azophenine, the structure determinations yielded straightforward evidence. The structure of the copper complex (Scheme 2) has been reported previously[11] (cf. also Table 2), the crystallographic data of the rhenium complex are given in Table 1. Figure 1 shows the structure of one of the two crystallographically independent but structurally very similar molecules *fac*-(L^o)Re(CO)$_3$Cl, experimental and DFT-calculated essential bond parameters are summarized in Table 2.

In both the copper and rhenium complexes the metal is coordinated to form a five-membered chelate ring involving the α-diimine part of L^o. The *o*-quinone form of the azophenine ligand is evident from the C–C bond lengths within the quinone ring and from the distances between ring carbon atoms and the nitrogen atoms. For both the copper(I)[11] and the rhenium(I) complex the average values are about 1.36 Å for the C–N bonds and 1.31 Å for the C=N bonds. Also in agreement with a recently published bond length pattern for *o*-quinonoid ligands in different oxidation states[25] the C=C bonds of coordinated L^o average at about 1.36 Å whereas the C–C distances lie at about 1.41 Å for the C^2–C^3 and C^6–C^1 bonds or at ca. 1.49 Å for the C^1–C^2 and C^4–C^5 bonds, respectively.

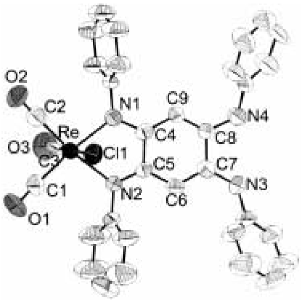


Figure 1. Molecular structure of [(L^o)Re(CO)$_3$Cl] in the crystal.

Unlike [(L^o)Cu(PPh$_3$)$_2$](BF$_4$) the non-ionic [(L^o)Re(CO)$_3$Cl] does not contain a free anion to coordinate with the two potentially chelating NHPh groups (Scheme 2). However, a closer inspection of the crystal structure reveals intermolecular hydrogen-bonding interactions between NHPh functions of one molecule and the rhenium-bound chloride ligand of the neighboring molecule, resulting in infinite chains. The average Cl–(H)N distances at 3.28 Å (Cl1–N3: 3.287 Å, Cl1–N4: 3.254 Å, Cl2–N7: 3.237 Å, Cl2–N8: 3.352 Å) support the presence of hydrogen bonding.[26] Apparently, the rather short calculated Cl–H(N) distances Cl2–H7 (2.303 Å) and Cl2-H8 (2.287 Å) for molecules 2 correlate with a considerable shortening of the Re2–C(O)$_{ax}$ bond to 1.843(14) Å and a lengthening of the Re2–Cl2 bond to 2.508(3) Å (Table 2). Typical Re–Cl distances in complexes of *fac*-[Re(CO)$_3$Cl] with acceptor ligands are about 2.47 Å.[27a]

Like the relatively long Re–C(O)$_{eq}$ bonds at about 1.92 Å the rather high carbonyl stretching frequencies confirm the strong π accepting character of L^o.[27] Generally, the experimental geometry of [(L^o)Re(CO)$_3$Cl] is reasonably well reproduced by the DFT calculations on the [(Meap)Re(CO)$_3$Cl] model complex (Table 2), slightly larger deviations for molecule 2 are attributed to the pertubation caused by stronger intermolecular hydrogen bonding.

A characteristic feature of the two complexes are very intense long-wavelength absorptions at 525 nm (Cu complex) and 567 nm (Re complex, Figure 2) in dichloromethane solution.

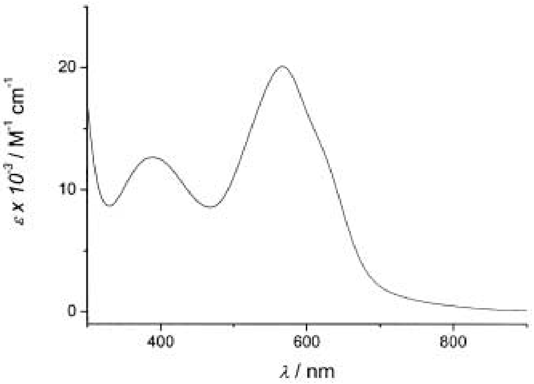
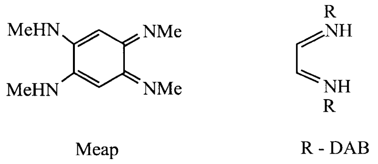


Figure 2. Absorption spectrum of [(L^o)Re(CO)$_3$Cl] in dichloromethane.

We attribute these absorptions to metal-to-ligand charge transfer (MLCT) transitions from d orbitals of the electron-rich metal centers with d^6 (Re^I) or d^{10} (Cu^I) configuration to the π* orbital of the *o*-quinonediimine π system which is largely concentrated at the coordinating α-diimine part. Such long-wavelength MLCT transitions have been observed for numerous α-diimine complexes of (Ph$_3$P)$_2$Cu$^+$ or [(OC)$_3$ClRe] with typical extinction coefficients ε of about 2000–4000 M^{-1}cm^{-1},[27–29] however, the very high intensities with $\varepsilon = 12500\,\text{M}^{-1}\text{cm}^{-1}$ for the Cu^I complex and even 20100 M^{-1}cm^{-1} for the Re^I compound of L^o is characteristic for complexes of *p*- and of *o*-quinonediimines as has been reported before mainly for ruthenium(II) compounds.[15] The second main band occurs at 395 nm (Cu complex) or 389 nm (Re compound) with $\varepsilon = 12000\,\text{M}^{-1}\text{cm}^{-1}$. Time-domain (TD-)DFT calculations for the *fac*-tricarbonylchlororhenium complex with the 7,8-dimethyl-4,5-bis(methylamino)-*o*-quinonediimine (Meap) model ligand (Scheme 3) confirm the MLCT identity and high oscillator strength of the long-wavelength transition (Table 3). The set of two closely lying highest occupied molecular orbitals (HOMO) is formed by MOs with large contributions from Re 5d orbitals interacting with 3p(π) orbitals of Cl. The LUMO of [(Meap)Re(CO)$_3$Cl] is formed by the π* orbital which is delocalized to large extent over the whole Meap ligand (Figure 3). The calculations allow us to assign the lowest



Scheme 3.

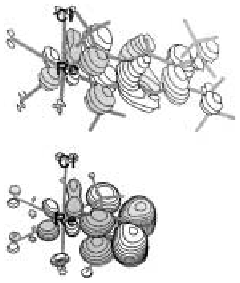


Figure 3. Shapes of the LUMOs of [(Meap)Re(CO)$_3$Cl] (top) and [(Medab)Re(CO)$_3$Cl] (bottom) complexes.

Table 3. Selected low-lying singlet excitation energies for [(N∩N)Re(CO)$_3$Cl].

State	Character	TD-DFT (N∩N = Meap) (B3LYP) Transition energy [eV][a]	Osc. str.	TD-DFT (N∩N = Meap) (HBandHLYP) Transition energy [eV][a]	Osc. str.	Experiment[b] (N∩N = L^o) λ_{max} [nm] (ε [M^{-1}cm^{-1}])
b^{1}A	MLCT/LLCT Re,Cl → Meap	1.98 (626)	0.105	2.44 (507)	0.217	567 (20100)[c]
c^{1}A	MLCT/LLCT Re,Cl→Meap	2.20 (563)	0.032	2.72 (456)	0.041	
d^{1}A	MLCT/LLCT Re,Cl→Meap	2.62 (473)	0.013	3.14 (394)	0.021	400 (12000)
e^{1}A	LLCT π(Cl)→π*(Meap), π→π*(Meap)	3.10 (399)	0.325	3.82 (324)	0.311	300 (23000)

[a] Wavelengths [nm] in parentheses. [b] From spectroscopy in CH$_2$Cl$_2$. [c] Shoulder at 630 nm.

lying transition to a HOMO-1 → LUMO excitation having mixed MLCT/LLCT character.

In order to reproduce and understand the unusually large intensity of this transition comparable TD-DFT calculations were performed on the complex [(Me-dab)Re(CO)$_3$Cl] (Table 4, Me-DAB = 1,4-dimethyl-1,4-diaza-1,3-butadiene).

Table 4. Selected low-lying singlet excitation energies for [(R-dab)Re(CO)$_3$Cl}.

State	Character	TD-DFT (R = Me) (B3LYP)		TD-DFT (R = Me) (HBandHLYP)		Experiment[b] (R = *t*Bu)
		Transition energy [eV][a]	Osc. str.	Transition energy [eV] [a]	Osc. str.	λ_{max} [nm] (ε [M^{-1}cm^{-1}])
a^{1}A′	MLCT/LLCT Re,Cl → Me-DAB	2.22 (558)	0.036	2.85 (435)	0.075	432 (2300)
b^{1}A′	MLCT/LLCT Re,Cl → Me-DAB	2.33 (532)	0.032	2.99 (414)	0.005	
e^{1}A′	LLCT π(Cl) → π*(Me-DAB), π → π*(Me-DAB)	3.45 (359)	0.325	4.28 (289)	0.067	

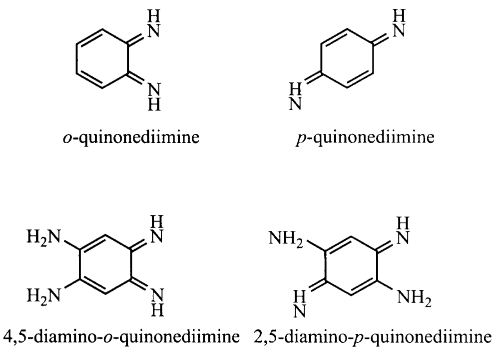
[a] Wavelengths [nm] in parentheses. [b] From spectroscopy in 1,2-dichloroethane.

Experimental data are available for [(*t*Bu-dab)Re(CO)$_3$Cl][27] and [(*i*Pr-dab)Re(CO)$_3$Cl].[28] In agreement with the experiments, the lowest transition within [(Meap)Re(CO)$_3$Cl] is calculated at a longer wavelength with the oscillator strength about three times larger in comparison with [(Me-dab)Re(CO)$_3$Cl], using the same functional. The transition moment of the lowest transition of the Meap complex is much larger due to the more delocalized LUMO (Figure 3). The second, less intense transition around 400 nm has a similar character as the lowest one, the next intense feature around 300 nm can be assigned to an LLCT transition (mixing of π(Meap) → π*(Meap) and p(Cl) → π*(Meap) transitions).

IR spectroscopy shows the presence of NH through bands at 3374 cm^{-1} (Cu complex, KBr) and 3288 cm^{-1} (Re complex, KBr), respectively. The ^{1}H NMR spectra exhibit H(NH) resonances at 7.96 ppm (Cu complex, CDCl$_3$) or 6.53 ppm (Re complex, CD$_2$Cl$_2$), the broader signal of the latter reflecting the absence of possible hydrogen bonding with an anion. Oxidation and reduction are irreversible for both systems at peak potentials of about +0.70 V and −1.25 V (Cu complex) or −1.05 V (Re complex, only reduction) versus (C$_5$H$_5$)$_2$Fe$^{+/o}$, respectively.

Since the rhenium complex demonstrates that metal-induced tautomerization of azophenine can occur also with non-ionic species we have explored the phenomenon of *p* → *o*-quinone ligand tautomerization at a more elementary level using DFT methodology. The possibility of a *p* → *o*-semiquinone isomerization has been discussed before in connection with the bis(2,2′-bipyridine)ruthenium(II) complex of deprotonated and semi-oxidized 2,4,5-trihydroxotoluene (a model of topasemiquinone, TPQ$^{\bullet-}$) which had shown well resolved EPR spectral features.[30]

DFT calculations on *o*/*p*-quinonediimines and their diamino forms (Scheme 4) show that the *p*-forms are more stable than the *o*-forms by 0.36 and 0.88 eV for quinonediimine and diamino-quinonediimine, respectively (Table 5). Contrary to the free ligands, however, the *o*-forms of all metal complexes with quinonediimines become more stable than the corresponding *p*-tautomers. Due to the interaction with metal cations, the *o*-forms of Li$^+$ and Cu$^+$ complexes with the diamino-quinonediimine are stabilized by about 0.37 eV in comparison with the *p*-forms (the stabilization is about 0.7 eV for unsubstituted quinonediimine complexes). Figure 4 shows the optimized structure of the Cu$^+$ complex of 4,5-diamino-*o*-quinonediimine, the complex with Li$^+$ has a similar structure. The calculated bond length Cu–N is 1.955 Å, the Li–N distance in the Li$^+$ complex is 1.941 Å.



Scheme 4.

Table 5. DFT (B3LYP) calculated free energies [eV] of quinonediimines and their complexes (Scheme 3).

	Free ligand	Li$^+$ complex	Cu$^+$ complex
o-quinonediimine	−9297.22	−9498.83	−53 928.85
p-quinonediimine	−9297.58	−9498.00	−53 928.29
o/*p*-difference	0.36	−0.83	−0.56
4,5-diamino-*o*-quinonediimine	−12 309.79	−12 512.08	−56 942.05
2,5-diamino-*p*-quinonediimine	−12 310.67	−12 511.70	−56 941.68
o/*p*-difference	0.88	−0.38	−0.37

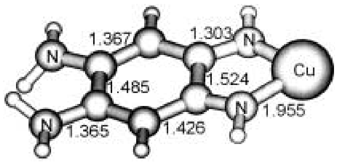


Figure 4. The optimized structure of the (4,5-diamino-*o*-quinonediimine)-copper(I) complex with calculated bond lengths in Å.

The metal-ion induced *p* → *o*-quinone tautomerism of azophenine is now well documented experimentally, also supported by DFT calculation results for more general systems. To approach the functional cooperation of metal and cofactor in amine oxidases we now plan to study the role of the second biochemical substrate, dioxygen. Preliminary experiments with azophenine and free copper(I) containing solutions in dichloromethane have shown that the admission of O_2 results in the bleaching of long-wavelength absorptions $\lambda > 1000$ nm which will be investigated further.

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