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Synthesis and Crystal Structure of Metal Complexes of N-phenyl-*o*-benzoquinonediimine (M = Ru^{2+}, Co^{3+}, Ni^{2+})

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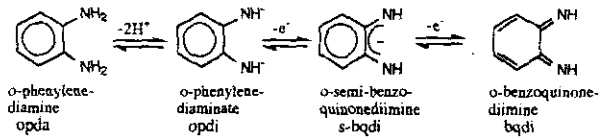
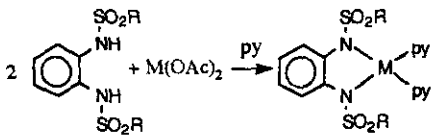
Electron-delocalized quinoid-like complexes — $[Ru^{II}(bipy)_2(N\text{-ph-bqdi})]^{2+}$, *cis*-$[Co^{III}(N\text{-ph-s-bqdi})_2(py)]^+$ and *trans*-$[Ni^{II}(N\text{-ph-s-bqdi})_2]$ (N-ph-bqdi = N-phenyl-*o*-benzoquinonediimine, N-ph-s-bqdi = N-phenyl-*o*-semi-benzoquinonediimine) were synthesized that display reversible multi-electron redox couples. The respective *cis*- and *trans*- conformation of the Co and Ni complexes are controlled by the steric effect of the substituent phenyl group. The Ni complex forms one-dimensional stacks in crystals. The crystal and molecular structures of three compounds are reported. $[Ru(bipy)_2(N\text{-ph-bqdi})](PF_6)_2$: space group $P2_1/c$, a = 13.292(2), b = 18.785(4), c = 13.959(2) Å; β = 97.42(1)°, V = 3456(1) Å^3, Z = 4, Rf = 0.047, Rw = 0.044; *cis*-$[Co(N\text{-ph-s-bqdi})_2(py)]\cdot(OAc)\cdot(H_2O)$: space group $P2_1/n$, a = 12.752(4), b = 13.303(2), c = 16.683(3) Å; β = 102.27(2)°, V = 2765(1) Å^3, Z = 4, Rf = 0.035, Rw = 0.035; and *trans*-$[Ni(N\text{-ph-s-bqdi})_2]$: space group P-1, a = 9.771(2), b = 10.417(1), c = 11.541(2) Å; α = 92.24(1), β = 104.04(1), γ = 117.94(1)°, V = 990.6(3) Å^3, Z = 2, Rf = 0.030, Rw = 0.031. Infrared, ^{1}H NMR, ^{15}N NMR and electronic absorption spectra, elemental analyses, magnetic and cyclic voltammetric data are presented.

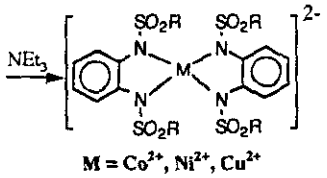
INTRODUCTION

Electron-delocalized complexes with ortho-semibenzoquinonediimine and ortho-benzoquinonediimine, shown below, play a main role in applications as pigments, photosensitizers and conductive materials.[1] Examples of such complexes are $[Re^{IV}(s\text{-bqdi})_3]^+$,[2] $[Fe^{II}(bqdi)_3]^{2+}$,[3] $[Ru^{II}(bipy)_2(bqdi)]^{2+}$,[4] $[Ru^{II}(bqdi)_2(opda)]^{2+}$,[5] $[Co^{III}(s\text{-bqdi})_2(py)]^+$,[6] $[M^{II}(s\text{-bqdi})_2]$ (M = Co,[3] Ni, Pd, Pt[7]), $[Cu^{II}(s\text{-bqdi})_2]$.[8]

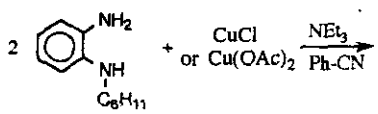


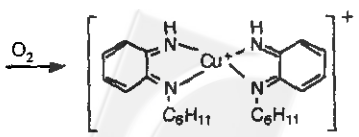
In our research, we devote much attention to complexes that have substituent groups on the nitrogen atoms of the ligands. Eq. (1) and eq. (2) show related reactions of two designed ligands N,N′-(*p*-tosyl)-opda and N-ch-opda (N,N′-(*p*-tosyl)-opda = N,N′-bis(*p*-toluenesulfonyl)-*o*-phenylenediamine, N-ch-opda = N-cyclohexyl-*o*-phenylenediamine) respectively. The former ligand has two strongly electron-withdrawing groups (-SO_2R); the latter has one electron-donating group (-C_6H_{11}). All these distorted tetrahedral complexes — $[Cu^{II}(N,N'\text{-}p\text{-tosyl-opdi})(py)_2]$,[6] $[Cu^{II}(N,N'\text{-}p\text{-tosyl-opdi})_2]^{2-}$[9] and $[Cu^{II}(N\text{-ch-bqdi})_2]^+$ [10] (N,N′-*p*-tosyl-opdi = N,N′-bis(*p*-toluenesulfonyl)-*o*-phenylene-diamine dianion, N-ch-bqdi = N-cyclohexylbenzoquinonediimine) are well characterized by X-ray crystallography.





(1)





(2)

Dedicated to Professor Sung-Mao Wang (王松茂) on the occasion of his seventieth birthday.

The substituent groups on nitrogen atoms of the ligands have a strong influence on the reaction system. Thus, the newly designed ligand — N-phenyl-opda and related complexes are introduced in this paper. Here we describe synthesis, structural, spectral and redox properties of three complexes — $[Ru^{II}(bipy)_2(N\text{-}ph\text{-}bqdi)](PF_6)_2$, *cis*-$[Co^{III}(N\text{-}ph\text{-}s\text{-}bqdi)_2(py)]\cdot(OAc)$ and *trans*-$[Ni^{II}(N\text{-}ph\text{-}s\text{-}bqdi)_2]$. The product of the coupling reaction of ligands — $C_{24}H_{19}N_4\cdot ClO_4$ is discussed.

EXPERIMENTAL SECTION

Physical Measurements

UV-vis spectra were measured on a spectrophotometer Hewlett-Packard 8452A. IR spectra were recorded of KBr pellets on a grating spectrophotometer Perkin-Elmer 983. ^{15}N NMR spectra were measured by the proton-inverse-detected ^{15}N NMR technique on instruments Bruker AMX-500 and AM-300 with nitromethane as standard. Magnetic susceptibilities were determined according to Gouy's method on a magnetic balance Cahn 7500 using $Hg[Co(SCN)_4]$ as the calibrant. Elemental analyses were performed on a Perkin-Elmer 240C instrument.

Electrochemistry

Acetonitrile (Fisher, spectral grade) was distilled from $KMnO_4$ and CaH_2. Tetrabutylammonium hexafluorophosphate (Janssen) was recrystallized and dried in *vacuo* at 100 °C. Cyclic voltammetry and constant potential electrolysis were performed on a potentiostat/digital coulometer EG&G Princeton Applied Research model 173/179 equipped with a universal programmer model 175. The working, reference and auxiliary electrodes were glassy carbon, Ag/AgCl and platinum respectively.

X-ray Structural Determination

Crystals of $[Ru(bipy)_2(N\text{-}ph\text{-}bqdi)](PF_6)_2$ were obtained by slow diffusion of diethyl ether into an acetonitrile solution of $[Ru(bipy)_2(N\text{-}ph\text{-}bqdi)](PF_6)_2$. Crystals of coupling ligand perchlorate salt $C_{24}H_{19}N_4\cdot ClO_4$ were obtained similarly. Crystals of *cis*-$[Co(N\text{-}ph\text{-}s\text{-}bqdi)_2(py)](OAc)(H_2O)$ were obtained by slow diffusion of diethyl ether into a pyridine solution. Crystals of *trans*-$[Ni(N\text{-}ph\text{-}s\text{-}bqdi)_2]$ were obtained from methanol solution by keeping the temperature at 0 °C for 12 h. Details of crystal parameters, data collection, and structural refinement are presented in Table 1. Raw intensities were collected on a Nonius CAD4 fully automated four-circle diffractometer with graphite-monochromatized Mo Kα radiation, using the $\omega/2\theta$ scan mode at 297 K with $2\theta_{max} = 50°$. Cell dimensions were obtained from 25 reflections with 2θ angle in the range 20.00-28.86°. All reflections were corrected for Lorentz, polarization and absorption effects. Data reduction and structural refinement were performed using the NRCC-SDP-VAX packages. The structures were determined by the Patterson method and refined by least squares; all non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included at idealized positions with a fixed contribution. $R_f = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $Rw = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$. Tables 2, 3, 4 and 5 list selected bond lengths and bond angles of the compounds — $[Ru(bipy)_2(N\text{-}ph\text{-}bqdi)](PF_6)_2$, *cis*-$[Co(N\text{-}ph\text{-}s\text{-}bqdi)_2(py)](OAc)(H_2O)$, *trans*-$[Ni(N\text{-}ph\text{-}s\text{-}bqdi)_2]$ and $C_{24}H_{19}N_4\cdot ClO_4$, respectively.

Materials

$Ru(bipy)_2Cl_2$ (Strem), $Co(OAc)_2$, $Ni(OAc)_2$, $Cu(ClO_4)_2\cdot 6H_2O$ (Merck), NEt_3 (Fluka) were used as purchased. The ligand N-ph-opda was prepared by a modification of the method of Ashon and Suschitzky.[11] All solvents and chemicals for syntheses were of reagent grade.

Syntheses

$[Ru^{II}(bipy)_2(N\text{-}ph\text{-}bqdi)](PF_6)_2$

To an aqueous solution (20 mL) of N-ph-opda (0.038 g, 2 mmol), $Ru(bipy)_2Cl_2$ (0.1 g, 2 mmol) was added. The resulting mixture was refluxed under N_2 for 2 h. NEt_3 (0.2 mL) was added to the mixture which was then further stirred under air at room temperature for 24 h. Upon addition of excess NH_4PF_6, a red-purple solid precipitated; it was filtered and washed with methanol (yield 60%). IR (cm^{-1}): 3298 (N-H), 1603, 1506, 1464, 1445, 842 (PF_6^-). ^{15}N NMR ($(CD_3)_2SO$) = -104.6 ppm (NH). UV-vis (CH_3CN) λ_{max} (nm) ($\log\varepsilon/(cm^*M)^{-1}$): 732br (2.70), 521 (4.24), 421sh (3.85). Diamagnetic. Anal. Calc. for $[C_{32}H_{26}N_6P_2F_{12}Ru]$: C, 43.36; H, 2.94; N, 9,49. Found: C, 43.11; H, 2.76; N, 9.88%.

***cis*-$[Co^{III}(N\text{-}ph\text{-}s\text{-}bqdi)_2(py)](OAc)(H_2O)$**

A mixture of N-ph-opda (0.29 g, 1.6 mmol) and $Co(OAc)_2$ (0.2 g, 0.8 mmol) in pyridine (20 mL) was stirred under air for 24 h. The deep blue crystals were formed directly by diffusion of diethyl ether into pyridine solution (yield 50%). IR (cm^{-1}): 3311 (N-H), 1585, 1549, 1521, 1460, 1422. UV-vis (CH_3CN) λ_{max} (nm) ($\log\varepsilon(cm^*M)^{-1}$): 764br (3.71), 587 (3.92), 464sh (3.82). Diamagnetic. Anal. Calc. for $[C_{31}H_{30}N_5O_3Co]$: C, 64.25; H, 5.18; N, 12.09. Found: C, 63.92; H, 5.26; N, 11.69%.

***trans*-$[Ni^{II}(N\text{-}ph\text{-}s\text{-}bqdi)_2]$**

To a methanolic solution (20 mL) of N-ph-opda (0.29 g, 1.6 mmol) and $Ni(OAc)_2$ (0.2 g, 0.8 mmol), NEt_3 (0.2 mL)

Table 1. Crystal Data and Data Collection Parameters for Benzoquinonediimine Complexes

Formula	$RuC_{32}H_{26}N_6P_2F_{12}$	$CoC_{31}H_{30}N_5O_3$	$NiC_{24}H_{20}N_4$	$C_{24}H_{19}N_4O_4Cl$
M(g/mol)	885.60	579.54	423.15	446.76
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
a/Å	13.292(2)	12.752(4)	9.771(2)	9.107(2)
b/Å	18.785(4)	13.303(2)	10.417(1)	9.863(4)
c/Å	13.959(2)	16.683(3)	11.541(2)	13.915(2)
α/deg	90	90	92.24(1)	74.85(2)
β/deg	97.42(1)	102.27(2)	104.04(1)	72.03(1)
γ/deg	90	90	117.94(1)	66.52(2)
U/Å^3	3456(1)	2765(1)	990.6(3)	1076.7(5)
Space group	$P2_1/c$	$P2_1/n$	P-1	P-1
Z	4	4	2	2
Dc/g cm^{-3}	1.702	1.392	1.419	1.378
μ/cm^{-1}	6.3	6.6	10.0	2.1
F(000)	1768	1200	440	480
Crystal size	0.10*0.10*0.30	0.35*0.40*0.60	0.25*0.30*0.55	0.10*0.15*0.30
Max., min. transmission	1, 0.951	1, 0.977	1, 0.914	1, 0.916
h,k,l range	-14 to 14	-15 to 14	-11 to 9	-9 to 10
	0 to 20	0 to 15	0 to 12	0 to 11
	0 to 15	0 to 19	-13 to 13	-15 to 16
Total no. of reflections	4502	4858	3486	3804
No. of unique reflections	4502	4858	3472	3789
No. of reflections used [$I > 2\sigma(I)$]	2317	3644	2786	1751
No. of parameters	478	390	274	298
Final R_f[a]	0.047	0.035	0.030	0.063
Final R_w[b]	0.044	0.035	0.031	0.060

[a] $R_f = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ [b] $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$

Table 2. Selected Bond Distances/Å and Angles/deg of $[Ru(bipy)_2(N\text{-ph-bqdi})](PF_6)_2$

Ru-N1	1.964(7)	Ru-N4	2.082(7)
Ru-N2	2.035(7)	Ru-N5	2.089(6)
Ru-N3	2.047(7)	Ru-N6	2.070(7)
N1-C1	1.312(11)	N6-C28	1.354(10)
N2-C6	1.308(11)	N6-C32	1.328(11)
N2-C7	1.423(10)	C1-C2	1.409(12)
N3-C13	1.338(12)	C1-C6	1.466(12)
N3-C17	1.368(11)	C2-C3	1.340(13)
N4-C18	1.366(11)	C3-C4	1.421(14)
N4-C22	1.323(12)	C4-C5	1.336(14)
N5-C23	1.336(11)	C5-C6	1.426(13)
N5-C27	1.345(10)		
N1-Ru-N2	77.6(3)	N2-Ru-N6	92.2(3)
N1-Ru-N3	91.8(3)	N3-Ru-N4	77.7(3)
N1-Ru-N4	91.0(3)	N3-Ru-N5	92.6(3)
N1-Ru-N5	175.1(3)	N3-Ru-N6	168.6(3)
N1-Ru-N6	98.1(3)	N4-Ru-N5	92.2(3)
N2-Ru-N3	95.3(3)	N4-Ru-N6	96.5(3)
N2-Ru-N4	166.5(3)	N5-Ru-N6	77.8(3)
N2-Ru-N5	99.73(25)		

Table 3. Selected Bond Distances/Å and Angles/deg of $[Co(N\text{-ph-s-bqdi})_2(py)](OAc)(H_2O)$

Co-N1	1.8522(21)	Co-N4	1.9399(20)
Co-N2	1.9291(20)	Co-N5	1.9921(22)
Co-N3	1.8357(20)	C1-C2	1.424(4)
N1-C1	1.312(3)	C1-C6	1.440(3)
N1-Hn1	0.850(22)	C2-C3	1.354(4)
N2-C6	1.341(3)	C3-C4	1.417(4)
N2-C13	1.434(3)	C4-C5	1.357(4)
N3-C7	1.317(3)	C5-C6	1.427(4)
N3-Hn3	0.828(21)	C7-C8	1.420(4)
N4-C12	1.341(3)	C7-C12	1.440(3)
N4-C19	1.442(3)	C8-C9	1.345(4)
N5-C25	1.337(3)	C9-C10	1.426(4)
N5-C29	1.339(3)	C10-C11	1.351(4)
C1-C2	1.424(4)	C11-C12	1.419(4)
N1-Co-N2	81.83(9)	N2-Co-N4	100.88(8)
N1-Co-N3	88.35(9)	N2-Co-N5	101.60(8)
N1-Co-N4	162.13(9)	N3-Co-N4	82.19(9)
N1-Co-N5	99.52(9)	N3-Co-N5	101.66(9)
N2-Co-N3	155.94(9)	N4-Co-N5	97.22(9)

Table 4. Selected Bond Distances/Å and Angles/deg of [Ni(N-ph-s-bqdi)$_2$]

Nia-N1a	1.8198(19)	Nia-N2a	1.8639(17)
N1a-C1a	1.333(3)	C2a-C3a	1.358(3)
N2a-C6a	1.355(3)	C3a-C4a	1.403(4)
N2a-C7a	1.426(3)	C4a-C5a	1.365(3)
C1a-C2a	1.408(3)	C5a-C6a	1.405(3)
C1a-C6a	1.431(3)		
N1a-Nia-N1a	180.0	N1a-Nia-N2a	96.46(8)
N1a-Nia-N2a	83.54(8)	N1a-Nia-N2a	83.54(8)
N1a-Nia-N2a	96.46(8)	N2a-Nia-N2a	180.0

Table 5. Selected Bond Distances/Å and Angles/deg of $C_{24}H_{19}N_4^+ClO_4^-$

N1a-C1a	1.327(7)	C5a-C6a	1.356(8)
N2a-C6a	1.383(7)	N1b-C1b	1.356(7)
N2a-C7a	1.415(7)	N2b-C6b	1.385(7)
C1a-C2a	1.387(8)	N2b-C7b	1.449(7)
C1a-C6a	1.465(7)	C1b-C2b	1.406(8)
C2a-C3a	1.384(8)	C1b-C6b	1.408(8)
C3a-C4a	1.451(7)	C2b-C3b	1.355(8)
C3a-N2b	1.363(7)	C3b-C4b	1.391(9)
C4a-C5a	1.424(7)	C4b-C5b	1.352(9)
C4a-N1b	1.317(7)	C5b-C6b	1.417(8)
C6a-N2a-C7a	128.1(5)	C4a-N1b-C1b	117.8(5)
C3a-N2b-C6b	121.4(4)	C3a-N2b-C7b	119.2(4)
C6b-N2b-C7b	119.4(4)		

was added. The resulting mixture was stirred for 3 h under air and filtered. Upon standing at 0 °C for 12 h, deep blue crystals were formed, which were filtered and washed with methanol (yield 70%). IR (cm^{-1}): 3336 (N-H), 3044 (C-H), 1570, 1531, 1477, 1440. ^{15}N NMR ((CD$_3$)$_2$SO) (ppm): -206 (NH). UV-vis (CH$_3$CN) λ_{max} (nm) (logε(cm*M)$^{-1}$)): 823 (5.62), 683 (4.39), 663 (4.75), 565 (4.46), 454 (4.49), 371 (5.02). Diamagnetic. Anal. Calc. for [$C_{24}H_{20}N_4Ni$]: C, 68.13; H, 4.73; N, 13.25. Found: C, 67.98; H, 4.67; N, 12.95%.

$C_{24}H_{19}N_4 \cdot ClO_4$

A mixture of excess N-ph-opda (1.98 g, 1.08 mmol) and Cu(ClO$_4$)$_2 \cdot 6H_2O$ (0.1 g, 0.27 mmol) in acetonitrile (20 mL) was stirred for 10 min and filtered. Purple crystals were formed directly by diffusion of diethyl ether into acetonitrile solution for several days (yield 30%). IR (cm^{-1}): 3369, 3235, 3068 (N-H), 1669, 1568, 1548, 1513 (vs), 1485, 1460, 1108 (vs), 1007 (ClO_4^-). Anal. Calc. for [$C_{24}H_{19}N_4 \cdot ClO_4$]: C, 64.46; H, 4.25; N, 12.53. Found: C, 64.29; H, 4.02; N, 12.84%.

RESULTS AND DISCUSSION

Structure and Spectra of [Ru^{II}(bipy)$_2$(N-ph-bqdi)](PF$_6$)$_2$

The structure of [Ru(bipy)$_2$(N-ph-bqdi)]$^{2+}$ is shown in Fig. 1. The Ru atom is bonded to the tris-bidentate ligand as a trigonally distorted octahedron. The diimine ligand N-ph-bqdi replaces one bipyridyl ligand of Ru(bipy)$_3^{2+}$,[12] with the original structure retained. The bite angles of the bidentate ligands are in the range 77.5°-78.5° for the three complexes Ru(bipy)$_3^{2+}$, Ru(bqdi)$_2$(opda)$^{2+}$ [5] and Ru(bipy)$_2$(N-ph-bqdi)$^{2+}$. N-ph-bqdi apparently indicates the quinoid instinct of the ring with localization of double bonds (average distance 1.338(14) (C2-C3, C4-C5) vs 1.431(25) Å for the other four single bonds). The relative strength of the metal to ligand back-π-bonding is proved by the coexisting presence of bipy and N-ph-bqdi in the coordination sphere of the Ru(II) complex. The bond lengths are 1.964(7) and 2.035(7) Å for Ru-N(1) and Ru-N(2) respectively and the average bond length of Ru-N(bipy) is 2.072(7) Å. The magnitude of back-π-bonding to both N-ph-bqdi and bqdi is therefore more significant than that to bipy. Basically, the two complexes Ru(bipy)$_2$(bqdi)$^{2+}$ and Ru(bipy)$_2$(N-ph-bqdi)$^{2+}$ show similar bond patterns.

Table 6 shows cyclic voltammetric data of [Ru(bipy)$_2$-(N-ph-bqdi)]$^{2+}$ in acetonitrile. Two reversible one-electron reduction couples at -0.38 and -1.05 V versus SCE were

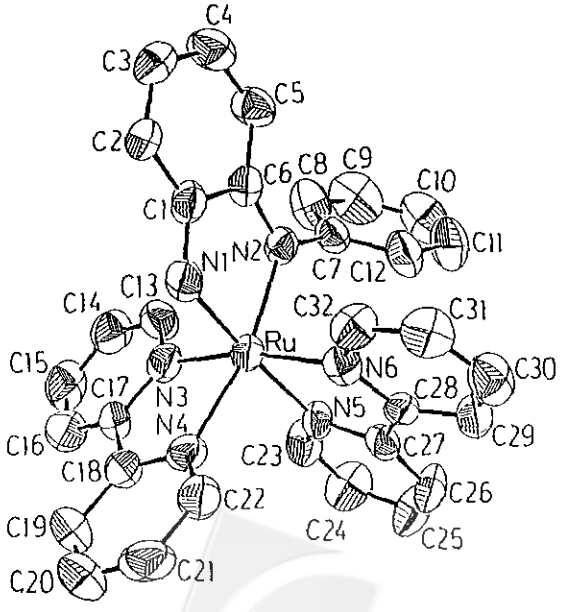


Fig. 1. Perspective view of [Ru^{II}(bipy)$_2$(N-ph-bqdi)]$^{2+}$ cation with atomic numbering.

Table 6. Electrochemical Reduction Potentials/V of Benzoquinonediimine Complexes

Species[a]	Ru^{+3}/Ru^{+2}	bqdi/s-bqdi	s-bqdi/opdi	bpy/bpy$^-$(1)	bpy/bpy$^-$(2)	solvent
$[Ru(bpy)_2(N\text{-ph-bqdi})]^{2+}$ [b]	+1.39	- 0.38	-1.05	-1.68[c]	-1.78[c]	CH_3CN
$[Ru(bpy)_2(bqdi)]^{2+}$ [d]	+1.35	- 0.47	-1.15[c]	-1.72[c]	-1.96[c]	CH_3CN
$[Ru(py)_4(bqdi)]^{2+}$ [d]	+1.33[c]	- 0.48	-1.24			CH_3CN
$[Ru(opda)(bqdi)_2]^{2+}$ [b,e]		- 0.32[f]				CH_3CN

Species[a]	bqdi/s-bqdi(2)	bqdi/s-bqdi(1)	opdi/s-bqdi(1)	opdi/s-bqdi(2)	solvent
$[Co(N\text{-ph-s-bqdi})_2(py)]^{+}$ [g,b]	+0.76	+0.35[f]	-0.08[h]	-0.55	CH_3CN
$[Co(s\text{-bqdi})_2]^{0}$ [i]	+0.61	- 0.17	-0.80	-1.83	DMSO
$[Ni(N\text{-ph-s-bqdi})_2]^{0}$ [b]		+0.23[f]	-0.69	-1.37	CH_3CN
$[Ni(s\text{-bqdi})_2]^{0}$ [i]		+0.23[f]	-0.88	-1.59	DMSO
$[Pd(s\text{-bqdi})_2]^{0}$ [i]	+0.78	+0.10	-0.89	-1.44	DMSO

[a] The valence charge is +2 for all metal ions except compound g. The labers 1 and 2 on bpy, opdi, s-bqdi, bqdi potentials refer to redox of the first and second ligand unit. [b] This work, $[TBA(PF_6)] = 0.1$ M, scan rate = 100 mV/s. [c] Quasi-reversible. [d] Ref. 13. [e] Ref. 5. [f] Pooly defined wave, irreversible reduction. [g] The valence charge is +3 for cobalt metal ion. [h] A litter split owing to py dissociation. [i] Ref. 7.

found. The additional chemically irreversible reduction couple in excess of -1.5 V results from formation of byproducts from highly reduced forms of the complex. Undoubtedly, the two steps corresponding to the ligand-centered reduction in which the benzoquinodiimine accepts an electron yield a semi-benzoquinonediimine ligand that progressively receives an electron to become an o-phenylenediamine dianion ligand. Electronic absorptions at 521 (d(Ru)→π*(N-ph-bqdi)) and 421 nm (d(Ru)→π*(bipy)) are comparable with values at 515 and 445 nm in $[Ru(bipy)_2(bqdi)]^{2+}$.[13] To sum up, the sequence of π* orbital energies is N-ph-bqdi < bqdi < bipy.

Structure and spectra of *cis*-$[Co^{III}(N\text{-ph-s-bqdi})_2(py)](OAc)(H_2O)$

The coordination geometry around the cobalt atom is square pyramidal with two basal N-ph-s-bqdi ligands and the axial pyridine (shown in Fig. 2). Two phenyl groups are simultaneously perpendicular to the s-bqdi rings and located at the same side. Average bond distances Co-N (N1, N3), N=C (N1-C1, N3-C7), and the conjugated C=C (C2-C3, C8-C9) are 1.844(2), 1.315(3), and 1.350(6) Å respectively; on the other side, the average bond distances Co-N (N2, N4), N=C (N2-C6, N4-C12) and of their relevant conjugated C=C are 1.935(8), 1.341(3) and 1.354(4) Å respectively. Because of the steric effect, the bonds of Co-N, N-C and adjacent C=C that are near the substitution group are longer.

Comparison of *cis*-$[Co(N\text{-ph-s-bqdi})_2(py)]^{+}$ with $[Co(s\text{-bqdi})_2py]^{+}$,[6] indicates that the bond patterns are similar except the orientation of the axial pyridine. Because the bond lengths of ligands are in the gray range between typical s-bqdi and bqdi, the valences of cobalt atom and coordinating ligands are ambiguous according to Xray structural analysis. Therefore, the electronic structure can be described as either Co^{3+} with bis-semi-benzoquinonediimine or Co^{+} with bis-benzoquinonediimine.

According to its voltammogram *cis*-$[Co(N\text{-ph-s-bqdi})_2(py)]^{+}$ in acetonitrile (Table 6) exhibits one reduction couple at -0.55V. The quasi-reversible one-electron couple at -0.8 V accompanied by a little split at -0.1 V is due to the lability of the axial pyridine. According to our early work on $[Co(s\text{-bqdi})_2(py)]^{+}$, the fact that the axial ligand is labile in CH_3CN or DMSO is proved by NMR spectra and by isolation of the final stable product — $Co(s\text{-bqdi})_2$. The stable one- and two-electron-reduced species-$[Co(N\text{-ph-s-bqdi})_2]^{0}$

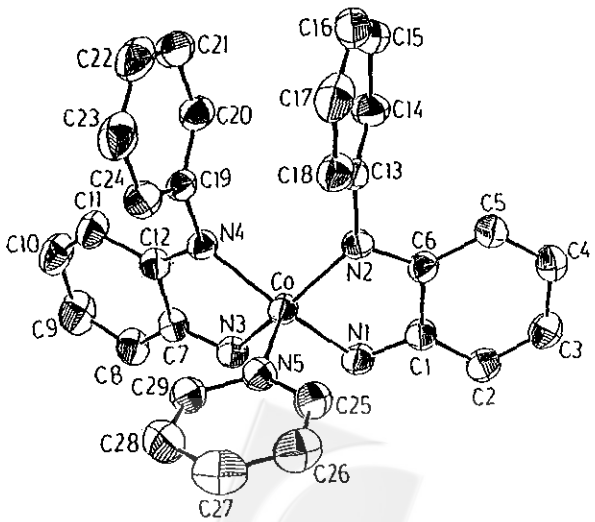


Fig. 2. Perspective view of $[Co^{III}(N\text{-ph-s-bqdi})_2(py)]^{+}$ cation with atomic numbering.

and $[Co(N\text{-ph-s-bqdi})_2]^{1-}$ were generated electrochemically.

Strructure and spectra of *trans*-$[Ni^{II}(N\text{-ph-s-bqdi})_2]$

The coordination geometry around the nickel atom is square planar with two N-ph-s-bqdi ligands (shown in Fig. 3). There are two independent molecules A and B in a lattice cell. The central nickel atom of the complexes forms one-dimensional stacks aligned along the b axis (shown in Fig. 4). For the A molecule, the bond distances Ni-N1, N1-C1 and of the related aromatic C2-C3 are 1.820(2), 1.333(3) and 1.358(3) Å respectively. On the opposite symmetric side, the bond distances Ni-N2, N2-C6, and relevant aromatic C5-C4 are 1.864(2), 1.355(3) and 1.365(3) Å respectively. The structures of *trans*-[Ni(N-ph-s-bqdi)$_2$] and [Ni(s-bqdi)$_2$] [14] are similar. In order to decrease its steric hindrance, the Ni complex exists in the trans comformation.

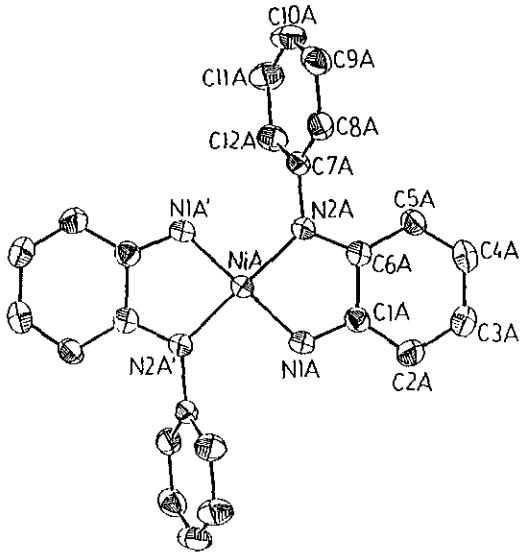


Fig. 3. Perspective view of $[Ni^{II}(N\text{-ph-s-bqdi})_2]^0$ with atomic numbering.

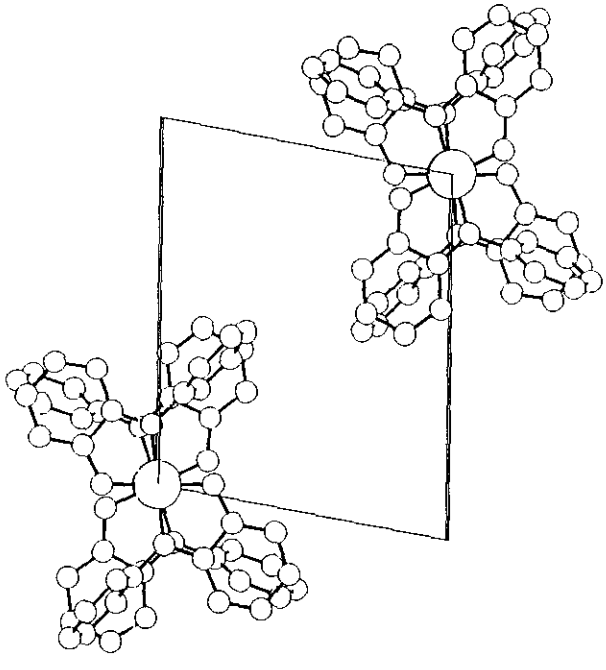


Fig. 4. View of the $[Ni^{II}(N\text{-ph-s-bqdi})_2]^0$ molecular one-dimensional stack and alignment with a axis packing in the crystal.

Cyclic voltammetry reveals two electrochemical reduction steps and one oxidation step in the nickel complex (see Table 6). Apparently, two reversible one-electron couples at -0.69 and -1.37 V have generated two species of Ni(N-ph-s-bqdi)(N-ph-opdi)$^-$ and Ni(N-ph-opdi)$_2^{2-}$. However, the irreversible two-electron couple at +0.3 V comes from ligand-center oxidation. The results indicate that the oxidized product Ni(N-ph-bqdi)$_2^{2+}$ is relatively unstable under the measured scan rate.

According to the theoretical investigation by both Zelewsky[15] and Lelj,[16] the exceptional spectra may be predominantly ascribed to the ligand character of the HOMO and LUMO orbitals. However, the substituent phenyl group can greatly influence the electronic transition from 780 nm for [Ni(s-bqdi)$_2$] to 823 nm for [Ni(N-ph-s-bqdi)$_2$].

Structure of $C_{24}H_{19}N_4 \cdot ClO_4$

Both N-ph-opda and opda have the same chemical behavior that leads to a coupling reaction of the ligands and produces 2,3-diamino-4,8-diphenylphenazine cation,[17,18] especially under the basic conditions with metal ions (Cu^{2+} ion produces the best yield). Resonance structures can be used to rationalize the bond patterns of this coupling product (shown below). The short bonds C1A-N1A, C5A-C6A,

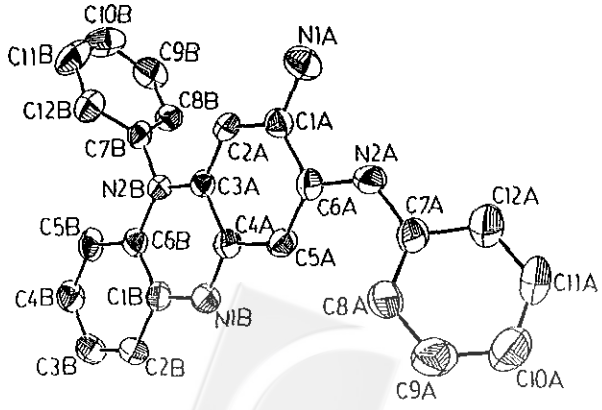
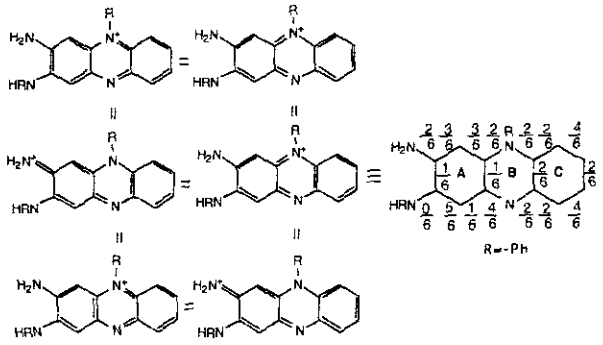


Fig. 5. Perspective view of $C_{24}H_{19}N_4^+$ cation with atomic numbering.

N1B-C4A, C3B-C2B and C4B-C5B indicate that they are inclined to double-bond character in the structure. Ring A is like a para-quinonediimine, and ring C is like an ortho-quinone diimine moiety.



SUMMARY

N-ph-opda and opda play analogous roles in reaction systems. Phenyl groups have no apparent electronic effect. They are distinct from alkylsulfonyl groups or alkyl groups in altering the oxidation states of ligands. From consideration of the bond patterns of these compounds, phenyl groups affect both the comformation of the complexes and molecular packing in the crystal. The red shifts of electronic absorption show better mixing of d(Ru)-π*(N-ph-bqdi) orbitals than that of d(Ru)-π*(bqdi) orbitals. To compare with well known metal complexes bipy and phen,[19] the quinoid-like electron-delocalized complexes deserve theoretical investigation.

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Supplementary Material

Tables of atomic coordinates, thermal parameters and structure factors are available from the authors upon request.

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Key Words

Ru(II); Co(III); Ni(II); Substituted benzoquinonediimine; Crystal structure.

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