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Synthesis of [M–N_4] and [M–N_6] Complexes Based on *o*-Benzoquinone Diimine with Cobalt, Iron, and Ruthenium

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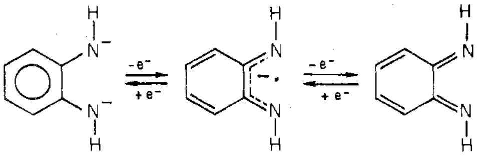
Procedures are outlined for preparing new derivatives of the *o*-benzoquinone diimine ligand system, *o*-$C_6H_4(NH)_2$, L, with cobalt, iron, and ruthenium by specific aerobic oxidations of appropriate *o*-phenylenediamine complexes. The isolated cobalt complexes consist of paramagnetic ($S = {}^1/_2$) $CoL_2{}^0$ and the diamagnetic CoL_2X (X = halide, SCN), $[CoL_2(PPh_3)]PF_6$, and $[CoL_3]PF_6$ derivatives. Iron forms stable diamagnetic $[FeL_3](PF_6)_2$, from which paramagnetic ($S = {}^1/_2$) FeL_2I and $[FeL_2(PPh_3)]PF_6$ are obtained. The isolated ruthenium complex is diamagnetic $[RuL_3](PF_6)_2$. The electrochemistry in acetonitrile and the spectral properties of these complexes are reported and compared with 2,2′-bipyridyl counterparts. The data suggest that *o*-$C_6H_4(NH)_2$ is one of the most effective α-diimine π acceptors with the result that reduced metal species are dramatically stabilized toward oxidation relative to those of bipyridyl.

Transition-metal complexes of the *o*-$C_6H_4(NH)_2$ ligand, a basic member of the α-diimine family of ligands, are of particular interest due to their oxidation–reduction propensities. The potential redox forms for the isolated donor molecule consist of the terminally reduced *o*-phenylenediamine dianion **1**, the *o*-benzosemiquinone diimine radical anion **2**, and the terminally oxidized neutral diimine, *o*-benzoquinone diimine, bqdi,[2] **3**. Electrochemical features of the only pure *o*-$C_6H_4(NH)_2$ complexes known to date, viz., the square-planar $M(bqdi)_2{}^z$ systems with M = Ni, Pd, Pt, and Co, were thoroughly investigated by Balch and Holm in 1966.[3a] These [M–N_4] complexes, like their [M–N_2S_2], [M–S_4], and [M–O_2S_2] analogues, were found to undergo multiple reversible one-electron-transfer reactions characteristic of this class of "suspect" or noninnocent ligand systems.[3b] A comparison of the redox potentials for a series of related $[Ni\text{–}X_2Y_2]^z$ complexes revealed that the N_4 donor set based on bqdi dramatically stabilizes the neutral and cationic (z = 0, +1, +2) members, whereas the sulfur donor analogues preferentially stabilize the anionic (z = −1, −2) and to a lesser degree the neutral (z = 0) species. As a result the electron-transfer series for the $M(bqdi)_2{}^z$ systems were found to be far more extensive than those of their sulfur counterparts, involving the formation of a number of unprecedented complexes. A particular example was found in $Co(bqdi)_2{}^0$ whose magnetic moment indicates a doublet ground state and a monomeric structure;[3a] the known $[Co\text{–}S_4]^0$ complexes, on the other hand, are dimeric and diamagnetic in both solution and the solid.[3b] Consequently, the coordination chemistry of bqdi with other metal ions might be expected to produce novel systems.



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Few other bidentate ligands possessing the α-diimine moiety,–N═C—C═N–, have hydrogen atoms on the nitrogen donor atoms. The relatively unhindered nature of the bqdi system enables two of these ligands to easily form a square-planar arrangement in a bis ML_2 system, a process which is difficult if not impossible with the more familiar heterocyclic 2,2′-bipyridyl (bpy) and *o*-phenanthroline[4] and with most other known neutral bidentate α-diimines.[5,6] As a consequence, the behavior of bqdi on nickel, palladium, platinum, and cobalt[3a] differs markedly from that of these latter ligands and provides further motivation for pursuing its coordination properties with other metal ions.[7] Herein are presented results of an extension of the chemistry of the bqdi ligand system with cobalt, iron, and ruthenium together with a comparison of related bpy systems.

Experimental Section

Preparation of Compounds. $Co[C_6H_4(NH)_2]_2$. Ten grams of cobaltous acetate tetrahydrate (40 mmol) dissolved in 200 mL of water was treated with 50 mL of concentrated aqueous ammonia and oxidized with a stream of air for ca. 2 h. The resulting deep brown solution was filtered to remove any insoluble material and treated with a filtered solution of 9.5 g (88 mmol) of practical grade *o*-phenylenediamine, opda, dissolved in 400 mL of warm water. After stirring of the mixture in an open beaker for ca. 18 h, the black solid which formed was filtered and washed well with water and with acetone until the washings were violet. The yield of crude $Co(bqdi)_2{}^0$ after drying was 6.4 g (60%). Purification was achieved by prolonged Soxhlet extraction with acetone under an atmosphere of nitrogen. Shiny, black, platelike crystals of the pure material eventually separated from the violet extract. An analytical sample was obtained by a second extraction under nitrogen.

$\{Co[C_6H_4(NH)_2]_3\}PF_6$. Ten grams of cobaltous acetate tetrahydrate (40 mmol) was oxidized in aqueous ammonia and treated with a solution containing 9.0 g of opda (83 mmol) and 10 g of NH_4PF_6 (60 mmol) in the same fashion as described above. After stirring of the mixture in the air for $5{}^1/_2$ h, the black microcrystalline powder was filtered, washed well with water (only), and dried in vacuo to yield 8.6 g (60%) of crude $[Co(bqdi)_3]PF_6$. Purification was achieved by Soxhlet extraction into dichloromethane, and the pure salt separated as a deep brown crystalline mass with a gold luster. It is very soluble in most polar solvents giving intense violet solutions, slightly redder than those of the neutral $Co(bqdi)_2{}^0$.

$Co[C_6H_4(NH)_2]_2I$. Aqueous Method. Following the $Co(bqdi)_2{}^0$ procedure, a solution of sodium iodide (1.1 mol/mol of Co) was added 10 min following the opda addition. After 7 h of stirring, the deep brown $Co(bqdi)_2I$ was obtained in 60% yield after washing with water and acetone (blue solution). Twice acetonitrile-extracted material was used for analytical purposes.

Nonaqueous Method. Under an atmosphere of nitrogen, 0.27 g (0.52 mmol) of dichloromethane-extracted $[Co(bqdi)_3]PF_6$ was stirred with 0.20 g (1.3 mmol) of NaI in 40 mL of dry tetrahydrofuran (THF) for 20 h; yield 0.17 g (83%) of $Co(bqdi)_2I$.

$Co[C_6H_4(NH)_2]_2SCN$. The aqueous procedure using NaSCN in place of NaI afforded crude dark brown $Co(bqdi)_2SCN$ in 47% yield. Two extractions with acetonitrile (violet solution) gave the pure crystalline material. The same compound was also obtained in an impure form in 74% yield by the nonaqueous procedure in 1,2-dimethoxyethane (DME). The solid shows sharp infrared bands at 2085 cm^{-1} (ν(CN)) and 720 cm^{-1} (ν(CS)?).

$Co[C_6H_4(NH)_2]_2Cl$. The chloro derivative was prepared by the nonaqueous procedure from $[Co(bqdi)_3]PF_6$ and LiCl (2 equiv) in 1,2-dimethoxyethane in 95% yield. The nearly black solid with a blue acetone solution decomposed during extraction–purification attempts, and its ^1H NMR spectrum in $Me_2SO\text{-}d_6$ contained low-intensity impurity resonances at δ ~12.7 and ~7.4.

$\{Co[C_6H_4(NH)_2]_2P(C_6H_5)_3\}PF_6$. Purified $[Co(bqdi)_3]PF_6$, 0.30 g (0.57 mmol), was stirred 18 h in 50 mL of dichloromethane containing 0.16 g (0.61 mmol) of triphenylphosphine. The deep brown-green mixture was filtered, and the black crystalline solid was washed with dichloromethane; yield 0.32 g (83%) of pure [$Co(bqdi)_2PPh_3$]PF_6. The salt is very soluble in polar organic solvents affording intense brown-green solutions.

Reduction of $Co[C_6H_4(NH)_2]_3{}^+$ to $Co[C_6H_4(NH)_2]_2{}^0$. Purified [$Co(bqdi)_3$]PF_6, 0.50 g (0.96 mmol), was stirred in 30 mL of THF with 1 equiv of 0.08% lithium amalgam for 30 min under an atmosphere of nitrogen. The solution–suspension was decanted from the mercury and filtered, and the dark microcrystalline compound washed with acetone; yield 0.155 g (60%) of $Co(bqdi)_2{}^0$. Elemental analysis and the electronic spectrum[3a] of the material established its identity, although there was slight contamination with mercury.

Iron(II) *o*-Phenylenediamine Complexes. (a) {$Fe[C_6H_4(NH_2)_2]_3$}$(ClO_4)_2$. An ethanolic solution, 50 mL, containing 4.7 g (43.5 mmol) of opda was treated at room temperature with 5.1 g (14 mmol) of solid $Fe(ClO_4)_2{\cdot}6H_2O$ under an atmosphere of nitrogen. The mixture was stirred for 30 min, cooled in an ice bath, and filtered in a Schlenk apparatus. The pale gray solid was washed with deoxygenated ethanol followed by toluene and dried in vacuo; yield 5.7 g (70%) of [$Fe(opda)_3$]$(ClO_4)_2$ as a gray, crystalline, air-sensitive solid. This material was not purified further and was stored under nitrogen in a refrigerator.

(b) $FeCl_2[C_6H_4(NH_2)_2]_2$. This material was prepared by refluxing 6.0 g (30 mmol) of $FeCl_2{\cdot}4H_2O$ with 3.3 g (30 mmol) of opda in 100 mL of 1-propanol under a nitrogen atmosphere. The off-white $FeCl_2(opda)_2$, 4.6 g (90%), was treated as described for the tris compound.

(c) $FeI_2[C_6H_4(NH_2)_2]_2$. Three grams (54 mmol) of iron powder was refluxed for 2 h under nitrogen in 150 mL of ethanol with 13.8 g (109 mmol) of iodine. The dark gray solution was then treated with 5.8 g (54 mmol) of opda and the mixture refluxed a further 3 h. The crude off-white $FeI_2(opda)_2$ was isolated as described above in 90% yield (12.6 g); the material is considerably more air stable than the tris or the chloro derivatives.

{$Fe[C_6H_4(NH)_2]_3$}$(PF_6)_2$. Twelve grams of Linde 4A molecular sieves was rapidly stirred (magnetically) with 1.0 g of $FeCl_2(opda)_2$ for 20 h in a mixture of dry dichloromethane (70 mL) and *tert*-butyl alcohol (70 mL) in a one-necked round-bottom flask fitted with a calcium chloride drying tube open to the air at one end. The resulting deep blue-green mixture was filtered, the residue was washed with methanol, and the combined filtrates were evaporated to dryness at room temperature on a rotary evaporator. The black residue was treated with ca. 20 mL of methanol and ca. 50 mL of water, the mixture was filtered, and the filtrate was treated with 2.8 g of NH_4PF_6 with stirring. The methanol was removed in vacuo, and the crude black salt was filtered and washed with 2-propanol until the washings were blue-green; yield 1.08 g (56%) of [$Fe(bqdi)_3$]$(PF_6)_2$.

Utilizing this same procedure, 1.7 g of [$Fe(opda)_3$]$(ClO_4)_2$ and 20 g of molecular sieves in 100 mL each of dichloromethane and *tert*-butyl alcohol afforded 1.09 g (56%) of the black $Fe(bqdi)_3{}^{2+}$ salt. Likewise, 1.8 g of $FeI_2(opda)_2$ (3.4 mmol), 15 g of sieves, and 0.46 g of opda (4.3 mmol) in 140 mL of the solvent mixture yielded 1.90 g of product (85%). An analytical sample was obtained by dissolving the crude material in ca. 1:5 methanol–water, filtering, and treating the filtrate with an excess of aqueous hexafluorophosphoric acid. The pure salt separated as fine black crystals with a red luster and was washed sparingly with 2-propanol.

$Fe[C_6H_4(NH)_2]_2I$. To 0.60 g (0.90 mmol) of purified [$Fe(bqdi)_3$]$(PF_6)_2$ dissolved in 20 mL of acetone were added 0.40 g (2.67 mmol) of NaI in 5 mL of acetone and a tiny crystal of *o*-phenylenediamine as catalyst. After stirring for 1 h the reddish mixture was filtered. The precipitate was washed with a small quantity of acetone followed by dichloromethane and toluene and was air-dried; yield 0.28 g (79%) of $Fe(bqdi)_2I$ as fine dark needles with a gold sheen. An analytical sample was obtained by Soxhlet extraction under nitrogen with dichloromethane, in which the compound is sparingly soluble.

{$Fe[C_6H_4(NH)_2]_2P(C_6H_5)_3$}$PF_6$. A mixture of 0.30 g (0.76 mmol) of $Fe(bqdi)_2I$ and 0.40 g (1.53 mmol) of triphenylphosphine was stirred together in 25 mL of methanol. Three grams (18.4 mmol) of NH_4PF_6 (previously placed in vacuo to remove traces of HF) was added to the deep red mixture which was stirred for ca. 20 min. The resulting dark crystalline solid was filtered, washed with toluene, air-dried, then washed with water, and dried in vacuo; yield 0.47 g (92%) of dark brown [$Fe(bqdi)_2PPh_3$]PF_6. An analytical sample was obtained by dissolving the compound together with a little PPh_3 in methanol at room temperature, filtering, and treating the filtrate with NH_4PF_6. The resulting crystalline solid was washed with water and toluene as above.

{$Ru[C_6H_4(NH)_2]_3$}$(PF_6)_2$. Under an atmosphere of nitrogen, 2.0 g (7.5 mmol) of hydrated ruthenium trichloride was refluxed with 7.3 g of opda (67 mmol) in 25 mL of water while zinc powder (ca. 0.2 g) was gradually added. The blue mixture was refluxed for 2 h, cooled, and poured into an open beaker. Approximately 300 mL of water and 10 mL of concentrated aqueous ammonia were added, and the suspension was stirred in the air for 16 h. The intense purple mixture was filtered and the solid treated again with dilute aqueous ammonia; this process was repeated with the filtered solids four times. Each of the purple filtrates was treated with a large excess (ca. 5 g) of NH_4PF_6, cooled in an ice bath, and filtered to remove the crude $PF_6{}^-$ precipitate. The combined precipitates were dissolved in warm water, reprecipitated with hexafluorophosphoric acid, and washed with 2-propanol to give a 7% yield, 0.37 g, of [$Ru(bqdi)_3$]$(PF_6)_2$ as fine dark brown crystals with a golden reflection. An analytical sample was obtained by elution chromatography from Sephadex SPC-25 with 0.2 M $NaNO_3$ and was twice precipitated from water as described above.

Physical Measurements. Conductivities were determined by use of a Philips GM4144 conductivity bridge. Electrochemical data were obtained by cyclic voltammetry (CV) on a PAR Model 170 electrochemistry system equipped with a three-electrode geometry. Acetonitrile was the solvent employed with 0.1 M tetraethylammonium perchlorate (TEAP) as supporting electrolyte; potentials were measured at a stationary platinum electrode vs. a saturated calomel electrode (SCE). Metal complex concentration was ca. 10^{-4}–10^{-3} M and the sweep rate 100 mV/s. Electronic spectra were measured on a Cary Model 118 recording spectrophotometer. The proton NMR spectra were recorded on a Varian HA-100 spectrometer. Magnetic susceptibilities were measured by the Faraday method on a Newport Instruments single-temperature Gouy balance using solid [$Ni(en)_3$]S_2O_3 as the calibrant. Mass spectra were recorded on an AEI MS902 instrument at 70 eV. EPR measurements were made with a Jeol JES-PE X-band spectrometer, utilizing a Jeol JM-PE-3 electromagnet. Analytical, spectral, and magnetic data for the bqdi complexes are summarized in Tables I–V.

Results

Synthesis and Characterization of bqdi Complexes. Free neutral *o*-benzoquinone diimine has never been isolated, although it is believed to be the initial transient deep red species from the reaction of *o*-phenylenediamine, *o*-$C_6H_4(NH_2)_2$, opda, with lead dioxide in organic solvents.[8] Only in a few instances, however, have solutions containing this compound been of synthetic utility in forming complexes, primarily from metal carbonyls.[3a,9] The usual procedure for preparing bqdi derivatives involves aerobic oxidation of the appropriate opda–metal complex in aqueous media, frequently in the presence of a base such as ammonia.[3a,10,11] While this aqueous oxidative dehydrogenation method was employed for the preparation of the neutral $M(bqdi)_2{}^0$ complexes of nickel, palladium, platinum, and cobalt,[3a] it was unsuccessful with a number of other metal ions, in particular with iron. Modifications of the published procedures were devised for the synthesis of new Co–, Fe–, and Ru–bqdi systems and are discussed individually for each metal.

(a) Cobalt Complexes. The known bqdi complexes of cobalt consist of spin-doublet $Co(bqdi)_2{}^0$ and diamagnetic $Co(bqdi)_2I$, which were described by Balch and Holm.[3a] These authors' procedure for the preparation of the neutral parent specified aerobic oxidation of cobaltous chloride in dilute ammonia solution to cobalt(III) prior to treatment with opda and subsequent stirring in air. The numerous attempts to repeat this procedure in our laboratory resulted in the formation of a sparingly soluble material with none of the chemical or spectral properties of the anticipated complex but rather with a resemblance to an undescribed oxidized derivative, $Co(bqdi)_2Cl$ (vide infra). Starting with cobaltous acetate, on the other hand, does consistently lead to the desired $Co(bqdi)_2{}^0$ complex in ca. 60% yields. Apparently the nature of the

Table I. Analytical, Conductance, and Magnetic Susceptibility Data for New bqdi Complexes

Compd	% calcd				% found				Λ, cm^2 mol^{-1} Ω^{-1}	μ_{eff}[a]
	C	H	N	M	C	H	N	M		
$[Co(bqdi)_3]PF_6$	41.40	3.47	16.09	11.28	40.82	4.33	15.42	11.64		Diamag
$Co(bqdi)_2Cl$	47.00	3.95	18.27		46.98	4.13	18.19			Diamag
$Co(bqdi)_2I$	36.21	3.04	14.07	14.80	36.71	2.99	14.05	14.61	25,[b] 19[c]	Diamag
$Co(bqdi)_2SCN$	47.42	3.67	21.27		47.77	4.00	21.54		24,[b] 11[c]	Diamag
$[Co(bqdi)_2PPh_3]PF_6$	53.11	4.01	8.26		53.28	4.25	8.10			Diamag
$[Fe(bqdi)_3](PF_6)_2$	32.55	2.73	12.65	8.41	32.60	3.52	12.30	8.08		Diamag
$Fe(bqdi)_2I$	36.49	3.06	14.18	14.14	36.32	3.45	14.23	14.03	20,[b] 8[c]	1.88
$[Fe(bqdi)_2PPh_3]PF_6$	53.35	4.03	8.30	8.27	52.51	4.11	8.08	8.69		2.17
$[Ru(bqdi)_3](PF_6)_2$	30.48	2.56	11.85		30.28	2.60	11.76			Diamag

[a] Data refer to solids at ~25 °C; diamagnetic susceptibilities not accurately measured. [b] Measured on freshly prepared ~0.5×10^{-3} M Me_2SO solutions at room temperature. In Me_2SO 1:1 electrolytes have conductivities in the range 23-42 cm^2 mol^{-1} Ω^{-1}: P. G. Sears, G. R. Lester, and L. R. Dawson, *J. Phys. Chem.*, **60**, 1433 (1956). [c] Measured on freshly prepared ~0.5×10^{-3} M CH_3CN solutions at room temperature. In CH_3CN 1:1 electrolytes have conductivities in the range 120-160 cm^2 mol^{-1} Ω^{-1}: W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).

Table II. Proton NMR Data for $[M\text{-}N_4]^z$ and $[M\text{-}N_6]^z$ bqdi Complexes

Compd	Solvent	Imine N-H resonance	C-H resonances
$Ni(bqdi)_2{}^0$	$(CD_3)_2SO$	8.80 (1, s)	6.96 (1, m), 6.68 (1, m)
$[Co(bqdi)_3]PF_6$	CD_3CN	11.31 (1, s)	7.47 (2, m)
$Co(bqdi)_2Cl$	$(CD_3)_2SO$	12.78 (1, s)	7.90 (1, m), 7.51 (1, m)
$Co(bqdi)_2I$	$(CD_3)_2SO$	12.50 (1, s)	7.76 (1, m), 7.25 (1, m)
$Co(bqdi)_2SCN$	$(CD_3)_2SO$	12.30 (1, s)	7.70 (1, m), 7.32 (1, m)
$[Co(bqdi)_2\text{-}PPh_3]PF_6$	CD_3CN	11.08 (1, s)	6.80-7.48 (~6, m)
$[Fe(bqdi)_3]\text{-}(PF_6)_2$	CD_3CN	11.66 (1, s)	7.03 (2, m)
$[Ru(bqdi)_3]\text{-}(PF_6)_2$	CD_3CN	11.96 (1, s)	7.04 (2, m)

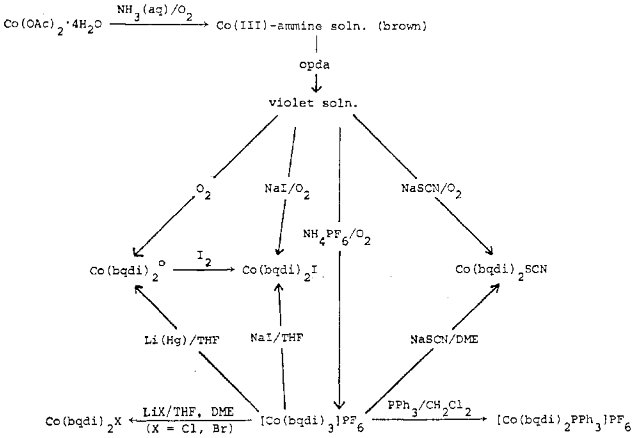
[a] Proton chemical shifts (δ) in ppm downfield (positive) from internal Me_4Si, measured at 100 MHz; integration, multiplicity in parentheses. Abbreviations: s, singlet; m, multiplet.

cobalt(II) counterion in this particular preparation is critical to the composition of the final product, a feature which was perhaps not recognized in the earlier work.[3a]

Addition of iodide ion to the oxidizing cobalt(III)-ammine/opda solution results in the formation of $Co(bqdi)_2I$, which had been previously prepared by halogenation of $Co(bqdi)_2{}^0$.[3a] Likewise, thiocyanate ion gives the new $Co(bqdi)_2SCN$ derivative by this procedure. These sparingly soluble diamagnetic compounds are purified by acetonitrile extraction, the blue iodo and the violet thiocyanato complexes being isolated as fine dark crystals with a gold sheen. Both $Co(bqdi)_2I$ and $Co(bqdi)_2SCN$ are 1:1 electrolytes in dilute Me_2SO solution and are nonelectrolytes and presumably five-coordinate in CH_3CN (Table I). The mass spectra of these compounds do not exhibit parent molecular ions but rather ions corresponding to *o*-benzoquinone diimine disproportionation products; for example, the ion of highest *m*/*e* observed with each complex corresponds to $CoC_{18}H_{14}N_6{}^+$, which may be formulated as cobalt containing one bqdi $C_6H_6N_2$ ligand and one 2,3-diiminophenazine $C_{12}H_8N_4$ ligand.[12] Other peaks in the mass spectra of these complexes correspond to $CoC_{12}H_{12}N_4{}^+$ ($Co(bqdi)_2{}^+$), $CoC_6H_6N_2{}^+$ ($Co(bqdi)^+$), $C_{12}H_{10}N_4{}^+$ (2,3-diaminophenazine(1+)), and $C_6H_8N_2{}^+$ (opda$^+$). The thermal disproportionation of these compounds seems to reflect their ionic character.

Inclusion of a large noncoordinating anion such as hexafluorophosphate in the final oxidation step of the aqueous preparation produces a new diamagnetic tris complex formulated as $[Co(bqdi)_3]PF_6$. In contrast to the previously described derivatives, this acid-sensitive water-insoluble salt is very soluble in polar organic solvents, forming intense violet solutions. Its ^1H NMR spectrum in acetonitrile solution is consistent with it formulation (Table II) and contains a broad singlet imine N-H resonance at δ 11.31.

Scheme I. Syntheses for the Co-bqdi Systems



The $Co(bqdi)_3{}^+$ ion is a useful starting material for the preparation of bis-ligand derivatives. One coordinated bqdi is readily displaced from this species in aprotic solvents by charged nucleophiles such as halide and thiocyanate ions to generate the sparingly soluble $Co(bqdi)_2X$ complexes.[13] The unstable chloride (X = Cl) obtained by this method closely resembles the material from the aqueous preparation starting with cobaltous chloride (vide supra); it decomposes during extraction-purification attempts. The uncharged nucleophile triphenylphosphine also displaces one bqdi from the tris complex in dichloromethane, forming diamagnetic black crystals with the formulation $[Co(bqdi)_2PPh_3]PF_6$.[14] This potentially five-coordinate complex is very soluble in polar organic solvents affording intense brown-green solutions. Finally, chemical or electrochemical reduction of the $Co(bqdi)_3{}^+$ ion generates the parent bis complex, $Co(bqdi)_2{}^0$. The reactions of the cobalt bqdi system are summarized in Scheme I.

The electronic spectra of these complexes, like those of the previously described $M(bqdi)_2{}^0$ systems,[3a] are very rich in the visible spectral region (Table IV), indicative of ligand-based electronic transitions. The ^1H NMR spectra of the diamagnetic systems (Table II) are normal, and all exhibit a characteristic broad singlet imine N-H resonance at low fields. In the solid state, their infrared spectra show sharp N-H stretches in the 3230-3440-cm^{-1} region. The electrochemistry of the parent $Co(bqdi)_2{}^0$ complex (Table III) in acetonitrile exhibits a reversible one-electron redox couple at -0.78 V vs. SCE corresponding to the $0 \rightleftarrows -1$ process and a quasi-reversible[15] one-electron step at -0.15 V for the $+1 \rightleftarrows 0$ transfer. This somewhat irreversible behavior of the latter couple suggests that the $Co(bqdi)_2{}^+$ cation may be strongly

Table III. Electrochemical Data for $[\mathrm{M{-}N_4}]^z$ and $[\mathrm{M{-}N_6}]^z$ Complexes[a]

Compd	Formal redox couples				
	$+3 \rightleftharpoons +2$	$+2 \rightleftharpoons +1$	$+1 \rightleftharpoons 0$	$0 \rightleftharpoons -1$	$-1 \rightleftharpoons -2$
$Ni(bqdi)_2^0$			+0.11	−0.84	(∼−1.4)
$Co(bqdi)_2^0$		(∼+0.4)[b]	−0.15*	−0.775	(∼−1.7)
$Co(bqdi)_2Cl$		(+0.32)[c]	−0.16*	−0.775	*d*
$Co(bqdi)_2I$		(+0.34)[c]	−0.185*	−0.775	*d*
$Co(bqdi)_2SCN$		(+0.42)[b]	−0.22*	−0.775	*d*
$[Co(bqdi)_2PPh_3]PF_6$		(+0.66)[b]	(−0.47)[f]	−0.78	*d*
$[Co(bqdi)_3]PF_6$		(+0.39)[b]	−0.15*	−0.775	*d*
$Fe(bqdi)_2I$		(+0.36)[e]	−0.36*	(−0.89)	
$[Fe(bqdi)_2PPh_3]PF_6$		(+0.50)[e]	−0.33*[g]	(−0.89)	
$[Fe(bqdi)_3](PF_6)_2$	+1.24	−0.15[h]	(∼−0.4)		
$[Fe(bpy)_3](BF_4)_2$	+1.08	−1.33[h]	(∼−1.5)		
$[Ru(bqdi)_3](PF_6)_2$	(+1.38)[i]	+0.03	−0.31	−1.08*	(∼−1.2)
$[Ru(bpy)_3](BF_4)_2$	+1.39	−1.31	−1.50	−1.76[j]	−2.4[j]

[a] Half-peak reduction potentials ($E_{\mathrm{p}/2}$) in V vs. SCE; measured in CH_3CN at stationary platinum by CV, sweep rate 100 mV/s; asterisks denote quasi-reversible couples; parentheses denote irreversible couples; all other couples are reversible unless otherwise noted. Reference 15 presents reversibility criteria. [b] Irreversible two-electron couple; half-peak oxidation potential reported. [c] Two closely spaced irreversible one-electron oxidation steps; half-peak oxidation potential of first step reported. [d] Not observed. [e] Half-peak oxidation potential. [f] This couple shifts to −0.54 V in the presence of excess PPh_3 and becomes somewhat more reversible ($\Delta E_\mathrm{p} = 90$ mV, $i_\mathrm{a}/i_\mathrm{c} = 0.89$ at 100 mV/s). [g] In the presence of excess PPh_3, this couple shifts to −0.41 V and becomes essentially reversible at 100 mV/s ($\Delta E_\mathrm{p} = 71$ mV, $i_\mathrm{a}/i_\mathrm{c} = 0.95$). [h] Reversible couple at rapid scan rates, $i_\mathrm{a}/i_\mathrm{c}$ decreasing at slower scan rates. [i] Irreversible multielectron (>2) oxidation step; half-peak oxidation potential reported. [j] Data from ref 23b; irreversible couple in this study.

Table IV. Electronic Spectral Data for Co–bqdi Systems[a]

$[Co(bqdi)_3]PF_6$	$Co(bqdi)_2Cl$	$Co(bqdi)_2I$	$Co(bqdi)_2SCN$	$[Co(bqdi)_2PPh_3]PF_6$
13.00 (10 000)	13.30 (5100)	13.32 (7600)	13.57 (8500)	14.04 (19 800)
				16.8 sh (2100)
17.83 (9600)	16.81 (9700)	16.47 (15 900)	17.86 (8600)	20.96 (8600)
		20.4 (4000)		23.6 sh (5300)
24.2 (900)	22.5 (1000)	24.1 (1700)	22.8 (1800)	
29.0 sh (500)	29.4 sh (900)		28.5 (300)	
34.5 sh (6400)	37.0 sh (7000)	38.5 sh (11 000)	33.3 sh (3700)	35.1 sh (6600)
40.65 (14 800)	39.68 (7400)	40.32 (12 300)	38.31 (7700)	40.32 (14 900)

[a] In acetonitrile solution; $\nu_{\max}$, $\mathrm{cm}^{-1} \times 10^3$ (ϵ).

solvated or ion-paired in this electrolyte medium.[16] Each of the $Co(bqdi)_3^+$, $Co(bqdi)_2X$, and $Co(bqdi)_2PPh_3^+$ derivatives undergoes more or less irreversible one-electron reductions to the parent $Co(bqdi)_2^0$ complex (which is identified by its characteristic reversible $0 \rightleftharpoons -1$ redox couple at −0.78 V). The potentials at which the tris species and the X = Cl, I, and SCN complexes reduce are within 70 mV of the $+1 \rightleftharpoons 0$ process for the parent; the substantial 320-mV cathodic shift for this couple with the triphenylphosphine system indicates stronger association of this ligand. Highly irreversible two-electron oxidation processes occur above +0.35 V with all these complexes, and the nature of the products is unknown.

(b) Iron Complexes. Balch and Holm were unable to prepare a bqdi complex with iron,[3a] the aqueous oxidation procedure failing due to the formation of insoluble ferric hydroxide. Likewise, aerobic oxidation of opda in the presence of anhydrous iron salts in alcohols, acetonitrile, or ethers affords only dark mixtures from which either ferric hydroxide eventually separates or no complex can be isolated. If, however, the readily prepared iron(II) derivatives $[Fe(opda)_3](ClO_4)_2$ or $FeX_2(opda)_2$ (X = halide ion) are stirred in dry air with 4A molecular sieves in a relatively noncoordinating solvent combination, viz., dichloromethane/*tert*-butyl alcohol, a deep blue-green mixture is produced from which an ionic complex can be isolated by precipitation from water with a large anion. The resulting diamagnetic, black crystalline hexafluorophosphate salt with the formulation $[Fe(bqdi)_3](PF_6)_2$ is isolated in 55–85% yields based on opda in the complexes. The new compound is moderately soluble in water and very soluble in polar organic solvents, giving intense blue-green solutions; its aqueous solutions are stable to acid but deposit ferric hydroxide in the presence of base. The ^1H NMR spectrum of the complex (Table II) exhibits an imine N–H resonance at δ 11.66; the electronic spectrum in Table V is compared with that of the well-known 2,2′-bipyridyl analogue $Fe(bpy)_3^{2+}$.

Table V. Electronic Spectra of Iron-Group bqdi and Comparable bpy Complexes[a]

Compd	Band max, $\mathrm{cm}^{-1} \times 10^3$ ($\epsilon_{\max}$)
$Fe(bqdi)_2I$[b]	16.86 (14 600), 18.01 (13 200), 19.84 (18 800), 21.7 sh (11 300), 25.8 sh (4200), 34.5 sh (7900)
$[Fe(bqdi)_2PPh_3]PF_6$[c]	15.63 (3300), 17.70 (7100), 20.79 (13 400), 24.81 (7950)
$[Fe(bqdi)_3](PF_6)_2$	14.26 (17 200),[d] 15.5 sh (15 800), 23.4 (2100), 34.5 sh (2700), 43.5 (25 000)
$[Fe(bpy)_3](BF_4)_2$	19.31 (8600),[d] 20.3 sh (7500), 24.3 sh (2400), 26.3 sh (3600), 28.74 (6500), 33.56 (60 000)
$[Ru(bqdi)_3](PF_6)_2$	14.9 sh (12 700), 15.24 (13 000),[d] 20.62 (22 900), 24.8 (4700), 45.5 (30 000)
$[Ru(bpy)_3](BF_4)_2$	22.32 (12 300),[d] 23.3 sh (10 600), 25.6 sh (4400), 28.8 sh (4900), 31.7 sh (9800), 34.97 (70 000)

[a] In methanol solution. [b] In 1,2-dichloroethane solution. [c] Run in the presence of excess PPh_3 to slow decomposition of complex. [d] More intense component of the "diimine band".

Electrochemical oxidation of the $Fe(bqdi)_3^{2+}$ complex in acetonitrile shows a reversible $+3 \rightleftharpoons +2$ redox couple at +1.24 V (Table III); the strongly oxidizing trication was not isolated in this study. A reversible $+2 \rightleftharpoons +1$ reduction is observed with $Fe(bqdi)_3^{2+}$ at −0.15 V, followed by an irreversible formal $+1 \rightleftharpoons 0$ process at ca. −0.40 V. Attempts to characterize these reduced species have been unsuccessful. The electrochemistry of the related $Fe(bpy)_3^{2+}$ complex is presented for comparison in Table III.

While conventional chemical or electrochemical techniques applied to the $Fe(bqdi)_3^{2+}$ complex failed to generate characterizable reduced systems, an unusual catalytic procedure was discovered which leads to a stable bis-ligand species formally derived from the tris dication by a one-electron reduction. Pure $[Fe(bqdi)_3](PF_6)_2$ is normally converted to the sparingly soluble iodide salt by treatment with sodium iodide in acetone solution. If, however, an unpurified hexafluorophosphate salt is used or a trace of opda is added, the initial blue-green mixture turns to a deep red color, and a sparingly soluble crystalline material with the formulation $Fe(bqdi)_2I$ separates in ca. 80% yield. This catalytic conversion does not appear to take place in other solvents, e.g., acetonitrile or ethers, and the mechanism is not known. The new air-stable iron complex forms deep wine red solutions (Table V) and is purified by dichloromethane extraction; it appears to be more soluble in nondonor solvents than its cobalt counterpart and has an infrared spectrum virtually coincident with that of the latter.

$Fe(bqdi)_2I$ is effectively a 1:1 electrolyte in dilute Me_2SO solution and a nonelectrolyte, probably five-coordinate, in CH_3CN (Table I). Unlike $Co(bqdi)_2I$, the ion of highest m/e observed in the mass spectrum of the iron complex corresponds to the parent ion of formula $FeC_{12}H_{12}N_4I^+$; other fragment ions correspond to $FeC_6H_6N_2I^+$ ($Fe(bqdi)I^+$) and $FeC_{12}H_{12}N_4^+$ ($Fe(bqdi)_2^+$). The room-temperature magnetic moment, μ_{eff} ($=\mu/\mu_B$) = 1.88 of $Fe(bqdi)_2I$ is compatible with a low-spin $S = {}^1/_2$ system; in a 1-chloronaphthalene glass at ~95 K the complex exhibits a rhombic EPR spectrum giving g values of 2.28, 2.11, and 2.02. Electrochemistry of $Fe(bqdi)_2I$ (Table III) shows three one-electron redox couples: an irreversible formal $+2 \rightleftarrows +1$ oxidation at +0.36 V, a quasi-reversible $+1 \rightleftarrows 0$ reduction at −0.36 V, and a further irreversible $0 \rightleftarrows -1$ reduction at −0.89 V.[15] Although there is no direct evidence bearing on the nature of the initial reduction product, it appears reasonable to formulate it as the uncharged $Fe(bqdi)_2^0$ or a solvated derivative thereof. The second reduction product may be $Fe(bqdi)_2^-$; however the irreversibility of the anodic portion of the cyclic wave suggests that it decomposes in the electrolyte medium. The identity of the oxidation product of $Fe(bqdi)_2I$ is not known.

Treatment of $Fe(bqdi)_2I$ with triphenylphosphine and ammonium hexafluorophosphate in methanol generates the potentially five-coordinate derivative $[Fe(bqdi)_2PPh_3]PF_6$. This paramagnetic compound has a room-temperature magnetic moment of $\mu_{eff} = 2.17$ and exhibits a simple low-spin rhombic EPR spectrum in a methanol–ethanol glass at ~95 K with resonances at g = 2.33, 2.07, and 2.00. The very soluble salt forms deep red solutions in most polar organic solvents (Table V); its infrared spectrum is very similar to that of the cobalt analogue. The electrochemical behavior of this complex (Table III) closely resembles that of the iodo derivative, featuring a quasi-reversible $+1 \rightleftarrows 0$ reduction at −0.33 V apparently to $Fe(bqdi)_2^0$, which itself exhibits a (characteristic) irreversible $0 \rightleftarrows -1$ couple at −0.89 V. The formal $+2 \rightleftarrows +1$ redox couple for $Fe(bqdi)_2PPh_3^+$ is shifted anodically relative to that of the iodo complex to +0.50 V; the nature of the oxidized species is unknown.

(c) Ruthenium Complex. The ruthenium analogue of the iron tris complex, $Ru(bqdi)_3^{2+}$, represents the first ruthenium bqdi system and is prepared by the aerobic oxidation of an aqueous ammoniacal suspension of the opda complex. The latter species, although not directly isolated, is generated by refluxing commerical ruthenium trichloride in water with an excess of opda in the presence of metallic zinc. The subsequent oxidation process forms a deep red-purple mixture from which the desired tris complex is selectively precipitated with hexafluorophosphate ion to give the diamagnetic intensely purple $[Ru(bqdi)_3](PF_6)_2$ salt in 7% yield. Its ^1H NMR spectrum (Table II) is consistent with the formulation; a single sharp N–H infrared stretching band at 3300 cm^{-1} is observed in the ruthenium complex as in the iron derivative. Table V compares the electronic spectra of this and the related $Ru(bpy)_3^{2+}$ system.

Unlike its iron counterpart, electrochemical oxidation of the $Ru(bqdi)_3^{2+}$ species is an irreversible multielectron process leading to disruption of the molecule. On the other hand, two reversible, one quasi-reversible, and one irreversible one-electron reductions[15] are observed in the $Ru(bqdi)_3^z$ system, corresponding to the $+2 \rightleftarrows +1$, $+1 \rightleftarrows 0$, $0 \rightleftarrows -1$, and $-1 \rightleftarrows -2$ couples, respectively. The electrochemical behavior of the analogous bpy system is also shown in Table III.

Discussion

(a) Bis Complexes of bqdi. Whereas the nickel-group $M(bqdi)_2^z$ systems possess more or less complete five-membered electron-transfer series,[3a] the corresponding M = Co and Fe series appear to be less complete and complicated by changes in ligation upon oxidation and reduction. This latter feature is indicative of metal oxidation state changes, giving rise to uncertainty in the electron distributions in the complexes and making the assignment of formal oxidation states misleading. The EPR spectra of $Fe(bqdi)_2I$ and $Fe(bqdi)_2PPh_3^+$, for example, are consistent with $S = {}^1/_2$ low-spin iron(III) in a rhombic field,[17a] and in the radical anion formulation **2** this would require spin coupling of the two bqdi ligands. On the other hand, the available data on the corresponding paramagnetic nickel species, $Ni(bqdi)_2^+$, support a nickel(II) formulation in which the unpaired electron is essentially ligand based.[3a]

The observed low-spin states for all of the isolated $(bqdi)_2$ complexes in this study, in particular for $Fe(bqdi)_2I$,[17b] are compatible with a very strong N_4 ligand field environment, which may be a reflection of the unconstrained nature of the o-$C_6H_4(NH)_2$ chelate and the small hydrogen substituents on the nitrogen donors. Single-crystal x-ray diffraction studies on $Ni(bqdi)_2^0$[18] and $Fe(CN)_4(bqdi)^{2-}$,[10] in fact, show the M–N distances to be among the shortest observed. Superficially, the $(bqdi)_2$ complexes resemble those of porphyrins, phthalocyanins, bis(glyoximes), and related tetraaza macrocycles, many of which are themselves "suspect" ligands.

The potentially coordinatively unsaturated iron, cobalt, and nickel $M(bqdi)_2^0$ species, which are of interest as regards their possible chemical reactivities toward oxygenation and oxidative addition, show a distinct metal-based dependence on their $+1 \rightleftarrows 0$ redox couples, the relative ease of oxidation in acetonitrile being in the order Fe (−0.36 V) > Co (−0.15 V) > Ni (+0.11 V). By contrast, their $0 \rightleftarrows -1$ couples occur within a relatively small potential range, −0.78 to −0.89 V (Table III).

(b) Tris Complexes of bqdi, bpy, and Other α-Diimine Ligands. The ionic species $Co(bqdi)_3^+$, $Fe(bqdi)_3^{2+}$, and $Ru(bqdi)_3^{2+}$ represent the first isolated tris complexes of bqdi. By contrast with the bis-ligand systems, o-$C_6H_4(NH)_2$ in its tris dicationic complexes of iron and ruthenium appears to behave as the neutral α-diimine **3**, as evidenced by similarities with the 2,2′-bipyridyl counterparts (Tables III and V). These systems are representative of a particularly stable complex type for low-spin d^6 iron(II) and ruthenium(II).[19] The neutral α-diimine bonding in a related bqdi complex of formal iron(II), the $Fe(CN)_4(bqdi)^{2-}$ ion, has been established by an x-ray structure determination[10] which demonstrates the localized alternating double-bond system **3** in the chelating ligand.[20] The air-stable cobalt complex $Co(bqdi)_3^+$, on the other hand, appears to be unique and to have no known α-diimine analogues; with bpy, for example, the tris di- and trications (containing formal cobalt(II) and -(III), respectively) are the stable members,[21] while the $Co(bpy)_3^+$ ion is reported to be strongly reducing and paramagnetic.[22]

Electrochemical comparison of the iron group $[M–N_6]^{2+}$ (M = Fe, Ru) analogues of bqdi and bpy is made in Table III.[23] Especially significant are the pronounced anodic potential shifts (>1.1 V) for the reduced $M(bqdi)_3^z$ couples relative to the corresponding $M(bpy)_3^z$ couples. This comparative ease of reduction of the o-$C_6H_4(NH)_2$ systems is compatible with a much greater acceptor character for the bqdi ligands, with the result that formally reduced species (based on the neutral donor) are dramatically stabilized toward oxidation relative to bipyridyl counterparts.

The electronic absorption spectra of the $Fe(bqdi)_3^{2+}$ and $Ru(bqdi)_3^{2+}$ complexes exhibit an intense low-energy, double-structured "diimine band",[24] which is characteristic with these d^6 tris(α-diimine) systems.[25] The band is considerably red-shifted with respect to that of its $(bpy)_3$ counterpart as shown in Table V. This type of absorption has been conventionally interpreted[19] as a metal to ligand charge-transfer transition involving filled metal d orbitals (of t_2 symmetry) and empty π^* (LUMO) orbitals of the ligands. Consequently, the energy of this transition has been taken as a relative measure of the π-back-bonding capacity of the respective α-diimine.[24] By this criterion, the "diimine band" positions for the iron and ruthenium $M(bqdi)_3^{2+}$ complexes indicate that o-$C_6H_4(NH)_2$ is a much more effective π acceptor than bipyridyl, and in fact surpasses nearly all the previously studied α-diimines in this regard.[24,26] The electrochemistry of these systems (vide supra) supports this interpretation of the spectral bands.[27]

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Registry No. $[Co(bqdi)_3]PF_6$, 63950-76-5; $Co(bqdi)_2Cl$, 63950-67-4; $Co(bqdi)_2I$, 63950-66-3; $Co(bqdi)_2SCN$, 63950-65-2; $[Co(bqdi)_2PPh_3]PF_6$, 63956-86-5; $[Fe(bqdi)_3](PF_6)_2$, 63950-78-7; $Fe(bqdi)_2I$, 63950-69-6; $[Fe(bqdi)_2PPh_3]PF_6$, 63950-80-1; $[Ru(bqdi)_3](PF_6)_2$, 63956-84-3; $Ni(bqdi)_2$, 14650-82-9; $[Fe(bqdi)_3](ClO_4)_2$, 63956-82-1; $Co(bqdi)_2$, 63950-68-5; $[Fe(bpy)_3](BF_4)_2$, 28966-86-1; $[Ru(bpy)_3](BF_4)_2$, 63950-81-2; $[Fe(opda)_3](ClO_4)_2$, 56390-52-4; $FeCl_2(opda)_2$, 21989-49-1; $FeI_2(opda)_2$, 22003-80-1; opda, 95-54-5.

References and Notes

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(2) In this paper the term o-benzoquinone diimine or bqdi is meant to refer to the o-$C_6H_4(NH)_2$ ligand system and not necessarily to distinguish between the various redox forms; the terminally oxidized form of the ligand has also been referred to as 1,2-diimino-3,5-cyclohexadiene and as o-phenylenediimine.

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(6) Well recognized negatively charged exceptions are the glyoxime type systems.

(7) For example, the solid-state electron transport properties of the stacked $M(bqdi)_2^z$ systems have only recently been examined: (a) J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.*, **20**, 99 (1976); (b) M. G. Miles and J. D. Wilson, *Inorg. Chem.*, **14**, 2357 (1975); (c) J. S. Miller, *ibid.*, **16**, 957 (1977). The potential of the coordinatively unsaturated $Co(bqdi)_2^0$ derivative as an oxygen carrier or as a vitamin B_{12} model is yet to be investigated.

(8) R. Willstätter and A. Pfannensteil, *Ber. Dtsch. Chem. Ges.*, **38**, 2348 (1905).

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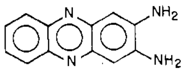
(10) G. G. Christoph and V. L. Goedken, *J. Am. Chem. Soc.*, **95**, 3869 (1973).

(11) Other preparative procedures for preparing bqdi and related derivatives in nonaqueous media are given by (a) M. M. Bagga, W. T. Flannigan, G. R. Knox, and P. L. Pauson, *J. Chem. Soc. C*, 1534 (1969); (b) T. R. Miller and I. G. Dance, *J. Am. Chem. Soc.*, **95**, 6970 (1973); (c) E. B. Fleischer and P. A. Tasker, *Inorg. Chim. Acta*, **6**, 72 (1972); also note the preparation of $Ni(bqdi)_2^0$ in ref 7b.

(12) Derived from 2,3-diaminophenazine, **4**, which is a common product of



4

the oxidation of o-phenylenediamine in the presence of transition metal ions.[7b]

(13) No apparent reactions occur with N_3^-, $CH_3CO_2^-$, NO_3^-, NO_2^-, or F^- ions; CN^- reacts, but without the formation of a precipitate.

(14) No apparent reactions occur with the neutral donors ethylene, carbon monoxide, or dimethyl sulfide.

(15) For reversible couples $\Delta E_p \approx 60–69$ mV and $i_a/i_c \approx 1$; for quasi-reversible couples $\Delta E_p \approx 100–350$ mV and $i_a/i_c \approx 1$; irreversible couples have larger peak potential differences and $i_a/i_c \neq 1$.

(16) The $+1 \rightleftarrows 0$ redox couple of the $Ni(bqdi)_2^z$ system appears reversible in acetonitrile by CV, suggesting that solvation or ion-pairing of the cation is not as pronounced as with $Co(bqdi)_2^+$. Unlike the reversible polarographic behavior observed in Me_2SO with the $-1 \rightleftarrows -2$ couples for these systems,[3a] these couples appear highly irreversible in acetonitrile by CV.

(17) (a) S. Koch, R. H. Holm, and R. B. Frankel, *J. Am. Chem. Soc.*, **97**, 6714 (1975), discussed EPR spectra of low-spin FeN_4X systems. (b) The related synthetic macrocyclic iron(III) complexes $Fe(Ph_2[14]N_4)SPh$[17a] and $Fe(Me_4[14]N_4)R$ (V. L. Goedken and Y. Park, *J. Chem. Soc., Chem. Commun.*, 214 (1975)) are apparently the only examples of doublet-state pyramidal iron(III) complexes.

(18) G. S. Hall and R. H. Soderberg, *Inorg. Chem.*, **7**, 2300 (1968).

(19) T. Ito, N. Tanaka, I. Hanazaki, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **41**, 365 (1968).

(20) The lack of such distinctive localization in $Ni(bqdi)_2^0$[18] suggests a different ligand formulation for this bis complex, most likely with some anionic character; E. I. Stiefel, J. H. Waters, E. Billig, and H. B. Gray, *J. Am. Chem. Soc.*, **87**, 3016 (1965), briefly discussed a molecular orbital scheme for this system.

(21) The $Co(bpy)_3^z$ system exhibits a reversible $+3 \rightleftarrows +2$ redox couple at +0.34 V, a quasi-reversible $+2 \rightleftarrows +1$ couple at −0.93 V, and two irreversible $+1 \rightleftarrows 0$ and $0 \rightleftarrows -1$ couples at −1.31 and −1.56 V in CH_3CN.

(22) W. R. McWhinnie and J. D. Miller, *Adv. Inorg. Chem. Radiochem.*, **12**, 135 (1969), mentioned references and a private communication regarding $Co(bpy)_3^+$.

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(26) A possible single exception to this is the related ligand 9,10-phenanthrenequinone diimine, which has its "diimine band" maximum at 13.93×10^3 cm^{-1}.[24]

(27) K. Schlosser and E. Hoyer, *Z. Anorg. Allg. Chem.*, **387**, 91 (1972), also provided some electrochemical data on related $Fe(\alpha\text{-diimine})_3^{2+}$ systems.