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Establishment of the Bond Patterns of *o*-Benzoquinonediimine and Semi-*o*-benzoquinonediimine: Crystal Structures of Metal Complexes, $[Fe^{II}(bqdi)_3](PF_6)_2$, $[Co^{II}(s\text{-}bqdi)_2]$ and $[Co^{III}Cl(s\text{-}bqdi)_2]$ *

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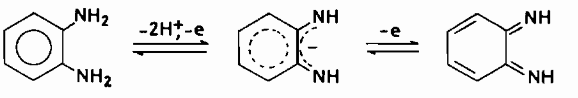
Transition metal complexes with delocalized ground state, *e.g.* the transition metal complexes of *o*-benzoquinonediimine (1, 2) [1] and diiminosuccinonitrile (3, 4) [2, 3], are of considerable interest owing to their unusual spectroscopic, magnetic, redox and structural properties.

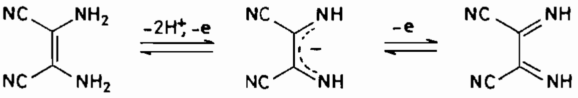


1 2

o-phenylene-diamine opda

semi-*o*-benzoquinonediime s-bqdi

o-benzoquinonediimine bqdi



3 4

diaminomaleonitrile damn

semi-diiminosuccinonitrile s-disn

diiminosuccinonitrile disn

1 and 3 usually form diamagnetic square planar complexes with d^8 metal ions [1–3], 2 and 4 form tris-α-diimine complexes with d^6 metal ions [4]. Early structural investigation of $[Ni(s\text{-}bqdi)_2]$ [7] suffered greatly from the twin crystal and film data, which prevented conclusive results regarding the extent of the delocalization in the ligand. Here we report the X-ray structural analyses of $[Fe^{II}(bqdi)_3](PF_6)_2$, $[Co^{II}(s\text{-}bqdi)_2]$, $[Co^{III}Cl(s\text{-}bqdi)_2]$ complexes and establish the bond patterns of the delocalized ligand in these complexes.

Reaction of the tris-opda iron(II) perchlorate with O_2 in dry CH_2Cl_2, followed by precipitation with PF_6^- from aqueous solution, leads to the isolation of diamagnetic, black crystalline compound, $[Fe(bqdi)_3](PF_6)_2$ [4]. Suitable single crystals (which are thf solvated and of green-black chunky appearance with a red luster) were obtained by slow diffusion of ether into a thf solution of $[Fe(bqdi)_3](PF_6)_2$.

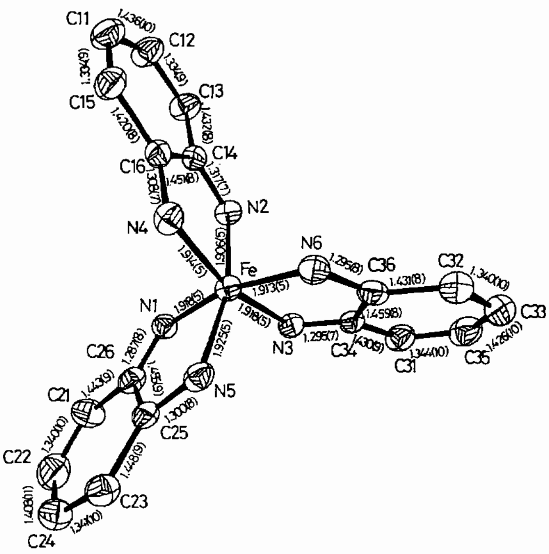


Fig. 1. ORTEP drawing of the cation $[Fe(bqdi)_3]^{2+}$ with 50% probability. Space group $P2_1/c$, a = 15.234(2), b = 10.144(2), c = 19.274(3) Å, β = 98.97(1)°, Z = 4, 2492 reflections with $I > 2\sigma(I)$, 398 parameters, R = 5.4%, R_w = 3.5%.

The result of the X-ray structural analysis of $[Fe(bqdi)_3](PF_6)_2\cdot(thf)$, shown in Fig. 1, indicates that the central iron atom has a trigonally distorted octahedral coordination. The 'bites' of the *o*-benzoquinonediimine ligands are such that the N–Fe–N angles are compressed from 90° to 79.4° and that the octahedron is trigonally twisted (~20°) along the three-fold axis. The very short iron–nitrogen distances (av. 1.916(5) Å) indicate very strong binding, associated with the low-spin iron(II) and the ligands of *o*-benzoquinonediimine.

The *o*-benzoquinonediimine ligand is planar. The six C=N bonds (av. 1.300(8) Å) and their conjugated six C=C bonds (av. 1.339(9) Å) are short, consistent with their identification as localized double bonds. The lengths of the remaining twelve C–C bonds (av. 1.437(10) Å) are only slightly shorter than those of the C–C single bonds in cyclooctatetraene (1.46 Å). The observed bond pattern of *o*-benzoquinonediimine ligand in this complex is very close to those in $[Fe^{II}(CN)_4(bqdi)]^{2-}$ [5], $[Ru^{II}(bqdi)(bipy)_2]^{2+}$ [6] and has a much more localized nature than that in $[Ni(s\text{-}bqdi)_2]$ [7].

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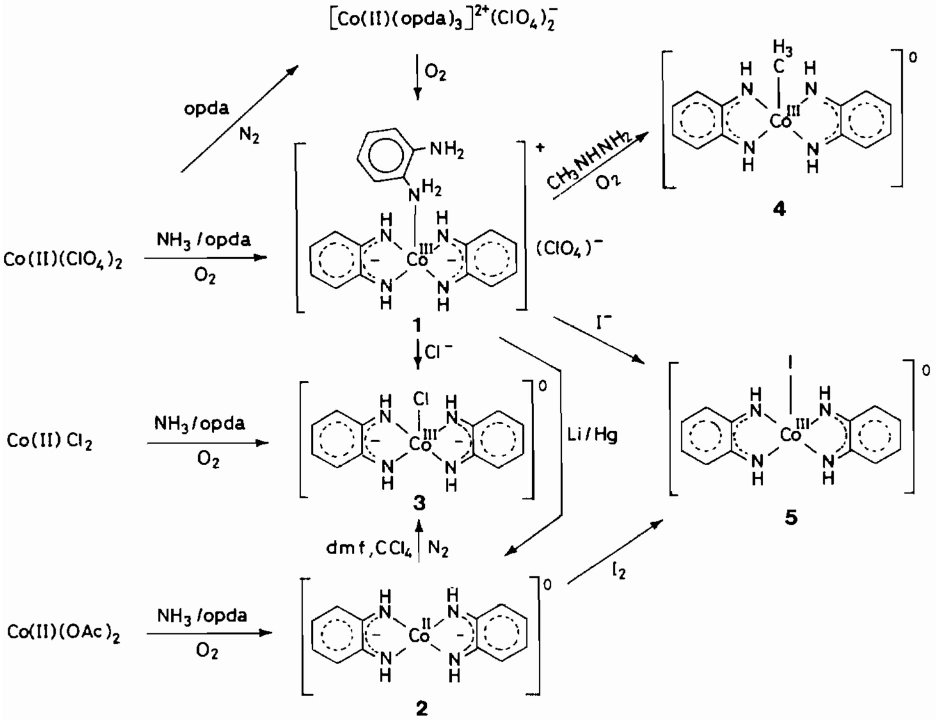

Scheme 1.

Cobalt complexes of *o*-benzoquinonediimine are complicated because of the presence of three possible oxidation states (I, II, III) and various coordination geometries. The characterization of $[Co(C_6H_4(NH)_2)_3](PF_6)$ in an early report [4] is doubtful*. The structural report on this complex cation in its BPh_4^- salt [8] also needs to be reinterpreted**. We present the corrected chemical transformations of cobalt complexes of *o*-benzoquinonediimine in Scheme 1 and report two novel structures of complexes **2** and **3** in this series.

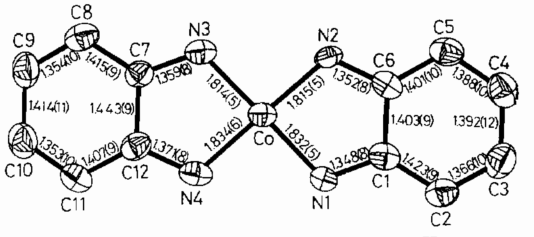

Fig. 2. ORTEP drawing of the molecule [Co^{II}(s-bqdi)$_2$] with 50% probability. Space group $P2_1$, a = 5.900(2), b = 7.460(3), c = 12.571(3), β = 91.62(3), Z = 2, 1014 reflections with $I > 2\sigma(I)$, 153 parameters, R = 4.4%, R_w = 4.8%.

The crystal structure of [Co^{II}(s-bqdi)$_2$], **2**, is given in Fig. 2 and is isomorphous with the nickel analogue [7]. The [Co(s-bqdi)$_2$] molecule is planar and the average Co–N bond length of 1.824(5) Å is short and comparable to the values in the metal complexes with delocalized ground state, *e.g.* [Ni^{II}(s-bqdi)$_2$], 1.83(1) Å [7], [Ni^{II}(s-disn)$_2$], 1.827(3) Å [9], [Co^{II}(s-disn)$_2$]$_2$, 1.85(1) Å [10] and [Co^{III}Cl(s-bqdi)$_2$], 1.857(9) Å (next paragraph). The bond pattern of the bqdi moiety is also similar in all of the above mentioned complexes, and has more delocalized double bonds than in the pure (or neutral) benzoquinonediimine complex, Fe^{II}(bqdi)$_3$](PF$_6$)$_2$.

For the crystal structure analysis of [Co^{III}Cl(s-bqdi)$_2$]·dmf, **3**, suitable single crystals were obtained by the slow reaction of [Co^{II}(s-bqdi)$_2$] with CCl$_4$ in dmf for two days. The result is shown in Fig. 3. The

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*The complex (1) is characterized as $[Co(C_6H_4(NH)_2)_3](PF_6)$ in ref. [4], but the correct formula should be $[Co(C_6H_4(NH_2)_2)(C_6H_4(NH)_2)_2](PF_6)$ from the following evidence: (a) The elemental analysis of $[Co(C_6H_4(NH_2)_2)(C_6H_4(NH)_2)_2]^+Y^-$: Y = PF_6^-, Found: C, 41.08; H, 3.75; N, 16.06. Calcd: C, 41.22; H, 3.82; N, 16.03%. Y = ClO_4^-, Found: C, 45.23; H, 4.18; N, 17.60. Calcd: C, 45.14; H, 4.17; N, 17.55%. Y = $BPh_4^-\cdot H_2O$, Found: C, 70.92; H, 5.73; N, 11.62. Calcd: C, 70.40; H, 5.87; N, 11.74%. (b) The multiple IR absorptions of these complexes in the N–H stretching region, 3390, 3300 and 3140 cm^{-1}, correspond to the stretching in amine NH$_2$ and imine NH. (c) The NMR spectrum of these complexes in d$_6$-dmso: imine NH resonance, 12.02, 12.36 (4H, s), aromatic CH, 7.30–7.80 (8H, m), 6.20–6.60 (4H, m) amine NH$_2$, 4.40, 4.12 (4H, s). The two kinds of imine NH are due to the partial dissociation of opda from the complex in dmso. (d) The bond lengths of this complex in ref. [9] can be interpreted as [Co^{III}(opda)(s-bqdi)$_2$]$^+$Y$^-$.

**The complex 1 is interpreted as [Co^{II}(s-bqdi)(bqdi)$_2$]$^+$ in ref. [9], but from the above arguments (ref. [8]), it should be interpreted as [Co^{III}(opda)(s-bqdi)$_2$]$^+$.

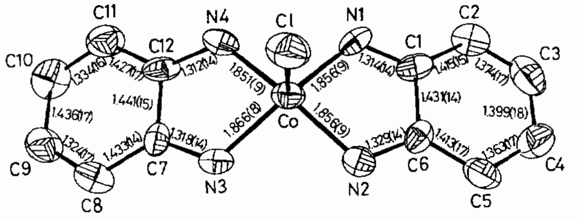

Fig. 3. ORTEP drawing of the molecule $[\mathrm{Co^{III}Cl(s\text{-}bqdi)_2}]$ with 50% probability. Space group $P2_1/c$, a = 13.062(8), b = 7.604(3), c = 15.571(11) Å, β = 108.87°, Z = 4, 1113 reflections with $I > 2\sigma(I)$, 208 parameters, R = 6.5% and R_w = 5.6%.

cobalt atom is 5-coordinated in square pyramidal geometry with one chlorine atom and four nitrogen atoms of the two *o*-benzoquinonediimine groups, and is displaced by 0.15 Å from the least-squares plane of the four donor atoms. The average Co–N distance and bond pattern of the *o*-benzoquinonediimine ligand in this complex are comparable to those in similar metal complexes with delocalized ground state, as discussed in the previous paragraph.

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