Inorganica Chimica Acta, *169* (1990) 19–21

Inorganica Chimica Acta
LETTER

Oxidations of *N*,*N*′-Disubstituted *o*-Phenylenediamine in the Presence of Metal Ions and the Crystal Structure of *N*,*N*′-Dimethylbenzimidazolium Perchlorate, Pyridine-bis(*o*-benzosemiquinonediimine)cobalt(III) Chloride and Bis(pyridine)(*N*,*N*′-bistoluene-*p*-sulfonyl-*o*-phenylenediiminato)-copper(II)

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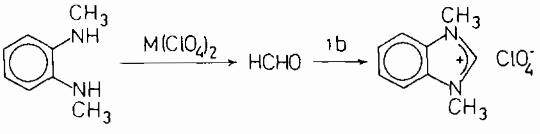
(Received December 6, 1989)

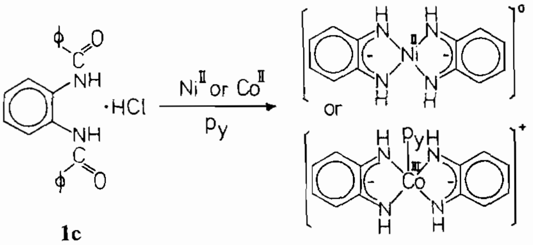
In continuing research on the metal complexes of *o*-benzoquinodiimine [1–4], we report the reactions of N,N′-disubstituted-*o*-phenylenediamine with metal ions under basic conditions, and the crystal structure of their products: *N*,*N*′-dimethylbenzimidazolium perchlorate, pyridine-bis(*o*-benzosemiquinonediimine)cobalt(III) chloride, and bis(pyridine)(*N*,*N*′-bistoluene-*p*-sulfonyl-*o*-phenylenediiminato)copper(II). The diamine molecules (1) can serve as bidentate or monodentate ligands [5]. They can be deprotonated to form dianions (2) and may be further oxidized to form anionic radicals (3) and neutral diimine molecules (4). Compound **3a** forms diamagnetic square-planar complexes with d^8 metal ions and **4a** forms tris-α-diimine complexes with d^6 metal ions.

The reactions of **1b** *N*,*N*′-dimethyl-*o*-phenylenediamine with $M(ClO_4)_2$ (M = Fe(II), Co(II), Ni(II), Cu(II)) in ethanol result in precipitates of various colours. Purification of these solids led to red crystals of *N*,*N*′-dimethylbenzimidazolium perchlorate. The benzimidazole is believed to form by the ring closure of *N*,*N*′-dimethyl-*o*-phenylenediamine with formaldehyde, which comes from the oxidative cleavage of the *N*-methyl group.

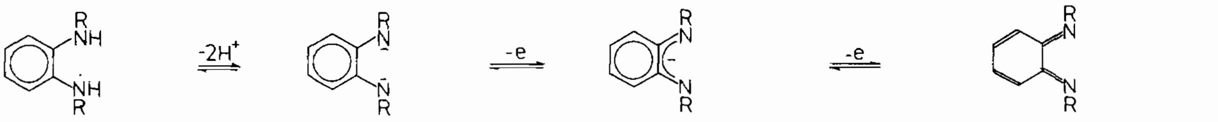


1b

The red crystals consist of *N*,*N*′-dimethylbenzimidazolium cations and perchlorate anions. The structure of the cation is shown in Fig. 1. The N1–C1 and N2–C2 bonds are short (1.31 Å) and exhibit partial double-bond character. The bond pattern is consistent with the proposed structure.



1c



N,*N*′-disubstituted
o-phenylenediamine
(opda)
1
1a, R = H
1b, R = CH_3
1c, R = $-C(=O)\phi$
1d, R = $-S(=O)_2-\text{tol}$

N,*N*′-disubstituted
o-phenylenediiminate
(opdi)
2
2a, R = H
2b, R = CH_3
2c, R = $-C(=O)\phi$
2d, R = $-S(=O)_2-\text{tol}$

N,*N*′-disubstituted
o-benzosemiquinonediimine
(s-bqdi)
3
3a, R = H
3b, R = CH_3
3c, R = $-C(=O)\phi$
3d, R = $-S(=O)_2-\text{tol}$

N,*N*′-disubstituted
o-benzoquinonediimine
(bqdi)
4
4a, R = H
4b, R = CH_3
4c, R = $-C(=O)\phi$
4d, R = $-S(=O)_2-\text{tol}$

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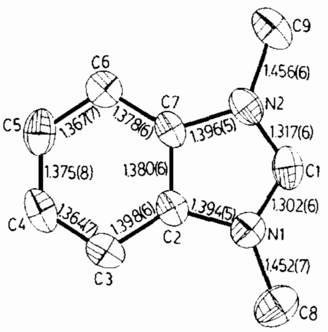

Fig. 1. ORTEP drawing of the *N,N'*-dimethylbenzimidazolium cation with 30% probability. Space group, *C*2/*c*; formula, $(C_9H_{11}N_2)^+ClO_4^-$: $a = 10.491(6)$, $b = 16.201(3)$, $c = 13.625(26)$ Å; $\beta = 106.2(1)°$, $Z = 8$. A total of 1218 reflections were observed with $I > 2\sigma(I)$, 145 parameters, to give $R = 5.6$, $R_w = 6.5\%$.

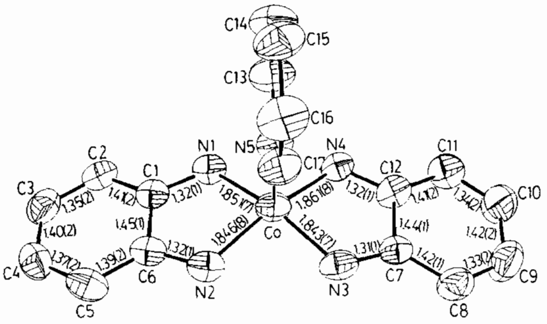

Fig. 2. ORTEP drawing of the cation $[Co^{III}(s\text{-}bqdi)_2py]^+$ with 50% probability. Space group, *C*2/*c*; formula, $[Co(C_6H_6N_2)_2(C_5H_5N)]^+Cl^-$: $a = 14.501(3)$, $b = 12.774(4)$, $c = 18.875(5)$ Å; $\beta = 93.98(2)°$, $Z = 8$. A total of 1024 reflections were observed with $I > 2\sigma(I)$, 370 parameters, to give $R = 3.4$, $R_w = 2.8\%$. Other pertinent bond parameters: Co–N5, 1.982(7) Å; N1–Co–C5, 98.7(3); N2–Co–N5, 101.2(3); N3–Co–N5, 101.4(3); N4–Co–N5, 97.3(3); N1–Co–N2, 82.0(3); N1–Co–N3, 159.8(3); N1–Co–N4, 95.4(3); N2–Co–N3, 94.1(3); N2–Co–N4, 161.5(3); N3–Co–N4, 82.0(3)°.

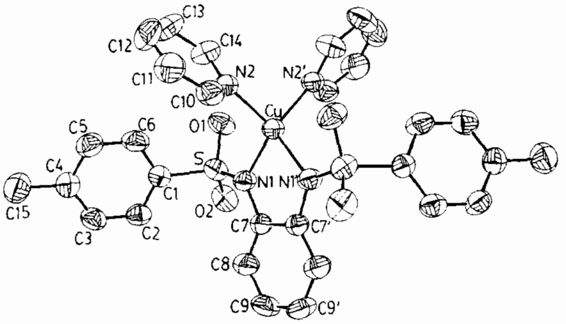

Fig. 3. ORTEP drawing of the molecule bis(pyridine)(*N,N'*-bistoluene-*p*-sulfonyl-*o*-phenylenediiminatocopper(II), $[Cu(py)_2(p\text{-toslopdi})]$, with 50% probability. Space group, *C*2/*c*: $a = 16.894(2)$, $b = 11.662(2)$, $c = 14.753(4)$ Å; $\beta = 100.62(2)°$, $Z = 4$. A total of 1599 reflections were observed with $I > 2\sigma(I)$, 242 parameters, to give $R = 3.5$, $R_w = 2.5\%$. Pertinent bond parameters: Cu–N1, 1.942(3); Cu–N2, 1.998(3); N1–S, 1.602(3); N1–C7, 1.399(5); S–O1, 1.442(3); S–O2, 1.439(3); S–Cl, 1.765(4); C7–C7', 1.403(7); C7–C8, 1.380(6); C8–C9, 1.372(7); C9–C9', 1.367(10) Å; N1–Cu–N1', 81.0(1); N1–Cu–N2, 128.8(1); N1–Cu–N2', 111.3(1); N2–Cu–N2', 98.7(1); Cu–N1–S, 117.5(2); Cu–N1–C7, 115.9(2); S–N1–C7, 124.9(3)°. $[M(py)_2(p\text{-toslopdi})]$ complexes with M = Co(II), Ni(II) or Cu(II) are all isomorphous.

The reactions of **1c** (*N,N'*-dibenzyl-*o*-phenylenediamine) with metal ions in pyridine resulted in hydrolysis of the amides and led to the isolation of the *o*-benzosemiquinonediimine metal complexes **3a**, e.g. $[Ni^{(II)}(s\text{-}bqdi)_2]$ and $[Co^{(III)}(s\text{-}bqdi)_2py)]^+$.

For the crystal structure analysis of $[Co^{(III)}(py)(s\text{-}bqdi)_2]^+Cl^-$, suitable single crystals were obtained by direct cooling of the reaction mixture of the hydrochloride salt of **1c** in hot pyridine with $Co(OAc)_2$. The result is shown in Fig. 2. The deep red–purple crystals consist of well-separated pyridine-bis(*o*-benzosemiquinonediimine)cobalt(III) cations and chloride anions. The cobalt atom is penta-coordinated in a square-pyramidal geometry with the nitrogen atom of pyridine in the axial site and four nitrogen atoms of the two *o*-benzosemiquinonediimine ligands in the equatorial plane, and is displaced by 0.314(4) Å from the least-squares plane of the four basal nitrogen atoms. The average Co–N distance and bond pattern of the *o*-benzosemiquinonediimine ligand in this complex are comparable to those in similar complexes, e.g. $[M^{II}(s\text{-}bqdi)_2]$, (M = Ni [6], Pd*, Pt*, Co [1]) and $[Co^{III}X(s\text{-}bqdi)_2]^+Y^-$ (X = Cl, Y = none [1]; X = opda, Y = $B\phi_4^-$ [7]).

The reaction of **1d** (*N,N'*-bistoluene-*p*-sulfonyl-*o*-phenylenediamine) with metal ions (M = Co(II), Ni(II), Cu(II)) in pyridine led to the isolation of the *o*-phenylenediiminate metal complexes **2d** $[M(R_2opdi)(py)_2]$ (M = Co(II), Ni(II), Cu(II); R = $SO_2C_6H_4CH_3$). UV–Vis spectroscopic data are: for Co(II), 588 nm ($\epsilon = 6.30 \times 10^2$ M^{-1} cm^{-1}), 576 (6.34×10^2), 520 (5.19×10^2), 386 (1.68×10^3), 306 (5.76×10^3); for Ni(II), 506 (1.23×10^2), 418 (2.22×10^2), 308 (4.79×10^3); for Cu(II), 820 (broad, 1.51×10^3), 526 (4.42×10^2), 312 (3.98×10^3).

The result of the X-ray structural analysis of $[Cu(R_2opdi)(py)_2]$, shown in Fig. 3, indicates that the central copper ion has a distorted tetrahedral coordination. The dihedral angle between the N1–Cu–N1' and N2–Cu–N2' planes is 74.46(14)°. The small Cu–N1 distance (1.942(3) Å) is attributed to

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*For $[M^{II}(s\text{-}bqdi)_2]$ with M = Pd, Pt. They are isomorphous with the Ni analogue (ref. 6) (unpublished result).

the negative charge of the nitrogen atom. The large C7–N1 distance (1.399(5) Å) and aromatic bond lengths in the C7–C8–C9–C9′–C8′–C7′ ring are consistent with the phenylenediiminate structure. This is the first report of the structure of a dianionic form of this series.

Acknowledgement

This work was supported by the National Science Council, Taiwan.

References

1 S. Peng, C. Chen, D. Liaw, C. Chen and Y. Wang, *Inorg. Chim. Acta, 101* (1985) L31.
2 S. Peng, K. Peters and A. Simon, *Inorg. Chim. Acta, 101* (1985) L35.
3 D. Liaw and S. Peng, *Inorg. Chim. Acta, 113* (1986) L11.
4 M. Hsieh, M. Cheng and S. Peng, *Inorg. Chim. Acta, 145* (1988) 1.
5 R. C. Elder, D. Koran and H. B. Mark, Jr., *Inorg. Chem., 13* (1974) 1644.
6 G. S. Hall and R. H. Soderberg, *Inorg. Chem., 7* (1968) 2300.
7 M. Zehnder and H. Löllige, *Helv. Chim. Acta, 63* (1980) 754.