New Coupling Reaction of *o*-Phenylenediamine Catalyzed by Mn(II) Ion

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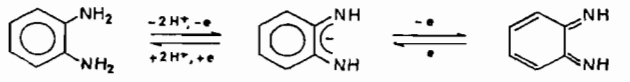
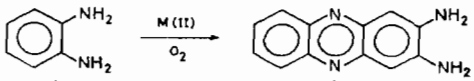
As a result of research on metal complexes with benzoquinonediimine (bqdi) and semi-benzoquinonediimine (s-bqdi) radical anion, a lot of work has been reported [1–6]. Balch and Holm well characterized the metal complexes (M = Co(II), Ni(II),



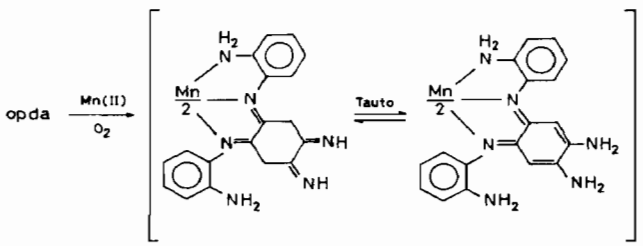
o-phenylene-diamine opda **1** | semi-benzoquinone-diimine s-bqdi **2** | benzoquinone-diimine bqdi **3**

Pd(II), Pt(II)) of **2** [1]. The crystal structure of [Ni(II)(s-bqdi)$_2$] has been reported by Hall and Soderberg [2]. Christoph and Goedken synthesized the Fe(II) complex of **3** and reported the structure of $[Fe(II)(CN)_4(bqdi)]^{2-}$ [3]. A series of interesting structures $[Fe(II)(bqdi)_3](PF_6)_2$, [Co(II)(s-bqdi)$_2$] and [Co(III)Cl(s-bqdi)$_2$] have been determined by us [4]. The dimerized coupling reactions of **1** catalyzed by transition metal ions have also been reported [5, 6].



1 **4**

We here report the new trimerized coupling reaction of **1** and the crystal structure of $[Mn(II)(tribqdi)_2](ClO_4)_2$ (**5**).



$[Mn(tribqdi)_2]^{2+}$ **5**

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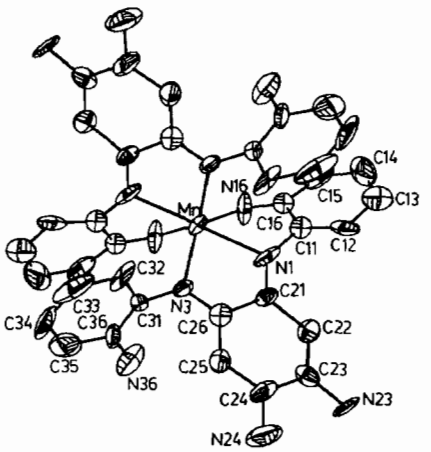

Fig. 1. ORTEP drawing of the cation $[Mn(tribqdi)_2]^{2+}$ with 50% probability. Space group $C2/c$, $a = 17.084(14)$, $b = 12.238(8)$, $c = 22.142(15)$ Å, $\beta = 104.13(5)°$, $Z = 4$, 1151 reflections with $I > 2.5\sigma(I)$, 253 variables, $R = 11\%$, $R_w = 11\%$. Complex ion lies on a crystallographic 2-fold.

The reaction of Mn(II) perchlorate with opda and O_2 in methanol solution for a few hours, followed by precipitation by adding diethyl ether, leads to the isolation of a dark green crystalline compound, **5**. Suitable single crystals were obtained by slow diffusion of ether into a methanol solution of **5**.

The result of the X-ray structural analysis of **5** shown in Fig. 1, and tabulated in Table I, confirms the trimerization of the oxidized opda ligand. The central Mn atom, located at crystallographic 2-fold, has a distorted octahedral coordination. The long Mn–N distances, 2.18(1), 2.25(1) and 2.34(2) Å indicate the high spin state of the complex and are attributed to the crowded coordination sphere. In the interesting tridentate ligand, the N1–C21 and N3–C26 distances, 1.23(2) and 1.33(2) Å respectively, are short, consistent with their identification as double bonds. The C22–C23, C23–N23, C24–N24 and C24–C25 distances are intermediate between those expected for the single and double bonds. The bond pattern of ring 2 is consistent with the hybrid of those of tetraimine and diimine-dienamine. The rings 1 and 3 are normal aromatic rings.

Supplementary Material

A table of coordinates and thermal parameters of **5** and a structure factor table of **5** are available from the authors on request.

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TABLE I. Bond Lengths (Å) and Bond Angles (°) of 5

Atom 1	Atom 2	Length	Atom 1	Atom 2	Length	Atom 1	Atom 2	Length
Mn	N1	2.25(1)	Mn	N1	2.25(1)	Mn	N3	2.18(1)
Mn	N3	2.18(1)	Mn	N16	2.34(2)	Mn	N16	2.34(2)
Cl	O1	1.43(2)	Cl	O2	1.39(2)	Cl	O3	1.36(2)
Cl	O4	1.35(2)	N1	C11	1.40(3)	N1	C21	1.23(2)
N3	C26	1.33(2)	N3	C31	1.40(3)	N16	C16	1.41(3)
N23	C23	1.34(2)	N24	C24	1.31(3)	N36	C36	1.40(3)
C11	C12	1.40(3)	C11	C16	1.40(3)	C12	C13	1.37(3)
C13	C14	1.42(4)	C14	C15	1.40(4)	C15	C16	1.34(4)
C21	C22	1.52(3)	C21	C26	1.46(3)	C22	C23	1.40(3)
C23	C24	1.45(3)	C24	C25	1.42(3)	C25	C26	1.46(3)
C31	C32	1.44(3)	C31	C36	1.35(3)	C32	C33	1.40(4)
C33	C34	1.38(4)	C34	C35	1.34(4)	C35	C36	1.41(3)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
N1	Mn	N1	156.5(7)	N1	Mn	N3	72.9(6)
N1	Mn	N3	93.3(6)	N1	Mn	N16	71.8(6)
N1	Mn	N16	128.7(6)	N1	Mn	N3	93.3(6)
N1	Mn	N3	72.9(6)	N1	Mn	N16	128.7(6)
N1	Mn	N16	71.8(6)	N3	Mn	N3	108.8(8)
N3	Mn	N16	134.4(6)	N3	Mn	N16	101.0(7)
N3	Mn	N16	101.0(7)	N3	Mn	N16	134.4(6)
N16	Mn	N16	80.0(7)	O1	Cl	O2	113(1)
O1	Cl	O3	109(1)	O1	Cl	O4	103(1)
O2	Cl	O3	106(1)	O2	Cl	O4	113(1)
O3	Cl	O4	113(1)	Mn	N1	C11	112(1)
Mn	N1	C21	116(1)	C11	N1	C21	132(1)
Mn	N3	C26	116(1)	Mn	N3	C31	127(1)
C26	N3	C31	116(1)	Mn	N16	C16	105(1)
N1	C11	C12	122(2)	N1	C11	C16	114(2)
C12	C11	C16	123(2)	C11	C12	C13	120(2)
C12	C13	C14	119(2)	C13	C14	C15	118(2)
C14	C15	C16	125(2)	N16	C16	C11	120(2)
N16	C16	C15	124(2)	C11	C16	C15	115(2)
N1	C21	C22	124(2)	N1	C21	C26	118(2)
C22	C21	C26	118(2)	C21	C22	C23	119(2)
N23	C23	C22	119(2)	N23	C23	C24	119(2)
C22	C23	C24	122(2)	N24	C24	C23	119(2)
N24	C24	C25	120(2)	C23	C24	C25	121(2)
C24	C25	C26	120(2)	N3	C26	C21	116(2)
N3	C26	C25	125(2)	C21	C26	C25	119(2)
N3	C31	C32	116(2)	N3	C31	C36	119(2)
C32	C31	C36	124(2)	C31	C32	C33	113(2)
C32	C33	C34	122(2)	C33	C34	C35	124(2)
C34	C35	C36	117(2)	N36	C36	C31	124(2)
N36	C36	C35	116(2)	C31	C36	C35	120(2)

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References

1 A. L. Balch and R. H. Holm, *J. Am. Chem. Soc., 88,* 5201 (1966).
2 G. S. Hall and R. H. Soderberg, *Inorg. Chem., 7,* 2300 (1968).
3 G. G. Christoph and V. L. Goedken, *J. Am. Chem. Soc., 95,* 3869 (1973).
4 S. M. Peng, C. T. Chen, D. S. Liaw, C. I. Chen and Y. Wang, *Inorg. Chim. Acta, 101,* L31 (1985).
5 M. G. Miles and J. D. Wilson, *Inorg. Chem., 14,* 2357 (1975).
6 S. M. Peng and D. S. Liaw, *Inorg. Chim. Acta, 113,* L11 (1986).