Crystal Structure of Manganese Picrate Complex with a New Binaphthylamide

Ya-Wen WANG,* Yan-Ling GUO,* Wei-Sheng LIU,*† and Da-Qi WANG**

*Department of Chemistry and State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000, People's Republic of China

**Department of Chemistry, Liaocheng University, Liaocheng, 252000, People's Republic of China

A solid complex of manganese picrate with *N*-methyl-2-{2'-[(methylphenylcarbamoyl)methoxy][1,1']binaphthalenyl-2-yloxy}-*N*-phenylacetamide, (L), was studied by X-ray diffraction methods. The molecular structure shows that the Mn (II) ion is six-coordinated by four oxygen atoms from the L and two from two unidentate picrates.

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Recent years have seen a considerable upsurge in interest in the chirality of coordination compounds.^{1,2} This can be ascribed to a number of factors: (i) the role of chiral metal complexes in asymmetric synthesis; (ii) advances in the field of bioinorganic chemistry; and (iii) the development of metallosupramolecular chemistry. Of the many chiral ligands developed for preparing chiral reagents and catalysts in asymmetric synthesis, 1,1'-2,2'-binaphthol (BINOL) is one of the most useful, and has made a considerable contribution to asymmetric synthesis.^{3,4} Recently, we synthesized a new binaphthylamide: *N*-methyl-2-{2'-[(methylphenylcarbamoyl)methoxy][1,1']binaphthalenyl-2-yloxy}-*N*-phenylacetamide, (L), and investigated the reaction of L with manganese picrate. As a subsequent study of such a complex, we give here its crystal structure.

A chemical diagram of the manganese complex is shown in Fig. 1. Also, the molecular crystal structure of the complex is illustrated in Fig. 2. A summary of the crystallographic data and details of the structure refinements are given in Table 1. Atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2. Selected bond lengths and angles are given in Table 3.

The manganese(II) ion is six-coordinated by four oxygen atoms from the L, two from two unidentate picrates. Due to the space obstacle, the two naphthalene rings in the molecule are

Fig. 1 Structure chemical diagram.

Table 1 Crystal and experimental data

Formula: C ₅₀ H ₃₆ MnN ₈ O ₁₈
Formula weight = 1091.81
Crystal system: monoclinic
Temperature = 293(2)K
Space group: C2/c
<i>a</i> = 22.879(5)Å
<i>b</i> = 14.881(5)
<i>c</i> = 14.773(4)
<i>V</i> = 4864(2)Å ³
<i>D_x</i> = 1.491 g/cm ³
No. of reflections used = 4301
2θ _{max} = 50.06° with Mo K _α
<i>R</i> = 0.0509
(Δ/σ) _{max} = 0.000
(Δρ) _{max} = 0.449 eÅ ⁻³
(Δρ) _{min} = -0.361 eÅ ⁻³
Measurement: Bruker SMART CCD
Program system: SHELXS-97
Structure determination: direct method
Refinement: full matrix least-squares

Fig. 2 Structure of [Mn(pic)₂L].

† To whom correspondence should be addressed.
E-mail: liuws@lzu.edu.cn

not vertical to each other, with a mean angle of 66.17° between the two rings. The distances between the Mn atom and the

Table 2 Atomic coordinates and equivalent isotropic displacement parameters for the title complex

Atom	x	y	z	U_{eq}
Mn(1)	5000	2325(1)	7500	44(1)
N(1)	3242(1)	3504(2)	6862(2)	54(1)
N(2)	5557(2)	169(3)	8565(2)	65(1)
N(3)	4066(2)	-1844(3)	9254(3)	76(1)
N(4)	3581(2)	1325(3)	8969(3)	75(1)
O(1)	4761(1)	3622(1)	8323(2)	42(1)
O(2)	4108(1)	2802(1)	6860(2)	47(1)
O(3)	4718(1)	1642(2)	8553(2)	66(1)
O(4)	5730(2)	911(3)	8415(3)	111(1)
O(5)	5839(2)	-489(3)	8541(3)	119(2)
O(6)	4431(2)	-2449(2)	9227(3)	102(1)
O(7)	3578(2)	-1964(3)	9400(3)	115(2)
O(8)	3251(2)	1221(3)	9491(3)	111(1)
O(9)	3524(2)	1951(2)	8446(3)	111(1)
C(1)	5154(1)	4341(2)	8601(2)	38(1)
C(2)	5196(1)	5019(2)	7993(2)	38(1)
C(3)	5643(2)	5709(2)	8313(2)	44(1)
C(4)	5737(2)	6424(2)	7735(3)	58(1)
C(5)	6170(2)	7056(3)	8065(3)	80(1)
C(6)	6538(2)	7009(3)	8986(3)	82(1)
C(7)	6467(2)	6330(3)	9547(3)	66(1)
C(8)	6022(2)	5655(2)	9236(2)	49(1)
C(9)	5959(2)	4925(2)	9819(2)	51(1)
C(10)	5532(2)	4289(2)	9507(2)	45(1)
C(11)	4126(1)	3809(2)	8125(2)	43(1)
C(12)	3823(1)	3337(2)	7228(2)	42(1)
C(13)	2899(2)	4087(2)	7311(2)	50(1)
C(14)	2919(2)	5000(3)	7208(3)	68(1)
C(15)	2597(2)	5544(3)	7655(4)	78(1)
C(16)	2240(2)	5189(3)	8172(3)	72(1)
C(17)	2214(2)	4275(3)	8268(3)	69(1)
C(18)	2548(2)	3725(3)	7851(3)	58(1)
C(19)	2915(2)	3047(4)	5994(3)	92(2)
C(20)	4590(2)	847(2)	8719(2)	49(1)
C(21)	4960(2)	67(2)	8731(2)	49(1)
C(22)	4788(2)	-789(2)	8902(2)	53(1)
C(23)	4239(2)	-925(2)	9091(2)	52(1)
C(24)	3859(2)	-221(3)	9120(3)	57(1)
C(25)	4023(2)	624(2)	8941(3)	53(1)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*(a_i\cdot a_j).$$

coordinated ether and carbonyl oxygen atoms are 2.417 Å and 2.139 Å, respectively, of which Mn-O (C=O) is shorter than Mn-O (C-O-C), indicating that the Mn-O (C=O) bond is stronger than the Mn-O (C-O-C) one. The coordination polyhedron is a distorted octahedron, which is probably due to

Table 3 Selected bond lengths (Å) and angles (°)

Mn(1)-O(1)	2.417(2)	Mn(1)-O(1)#1	2.417(2)
Mn(1)-O(2)	2.139(2)	Mn(1)-O(2)#1	2.139(2)
Mn(1)-O(3)	2.093(3)	Mn(1)-O(3)#1	2.093(3)
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O(1)-Mn(1)-O(1)#1	74.06(10)	O(2)#1-Mn(1)-O(2)	141.30(12)
O(2)-Mn(1)-O(1)#1	79.98(8)	O(2)#1-Mn(1)-O(1)	79.98(8)
O(2)-Mn(1)-O(1)	69.21(8)	O(2)#1-Mn(1)-O(1)#1	69.21(8)
O(3)-Mn(1)-O(2)	92.85(10)	O(3)#1-Mn(1)-O(2)#1	92.85(10)
O(3)-Mn(1)-O(1)	82.03(9)	O(3)#1-Mn(1)-O(1)#1	82.03(9)
O(3)-Mn(1)-O(1)#1	156.06(10)	O(3)#1-Mn(1)-O(1)	156.06(10)
O(3)#1-Mn(1)-O(2)	105.78(10)	O(3)-Mn(1)-O(2)#1	105.78(10)
O(3)-Mn(1)-O(3)#1	121.90(16)		

Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, y, -z + 3/2$

the interaction of the Mn atom and the O(4) atom. The corresponding distance between the Mn atom and the O(4) atom is 2.810 Å. The interaction might have some connection with the wide angle at O(3)-Mn-O(3)^{#1} of 121.9(2)° and the planarity of the picrate. The picrate ring is almost planar; the angles between the C20-C25 plane and the N3-O6-O7, N2-O4-O5 and N4-O8-O9 planes are 0.00, 0.00, 32.58°, respectively.

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