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Manganese(II) Bromide Coordination toward the Target Product and By-Product of the Condensation Reaction between 2-Picolylamine and Acenaphthenequinone

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Abstract: A heteroleptic binuclear manganese complex was obtained and characterized by single-crystal X-ray diffraction. Manganese ions coordinate with the target product and by-product of the condensation reaction between 2-picolylamine and acenaphthenequinone are characterized by different geometries in the resulting complex.

Keywords: alkyl-BIAN; picolylamine; manganese; condensation reaction; acenaphthenequinone; X-ray structure

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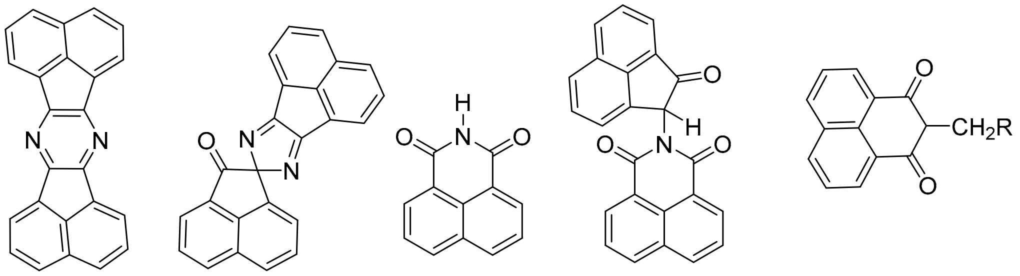
1. Introduction

Transition metal complexes with bis-iminoacenaphthenes (BIANs) are found in application in different areas of modern chemistry [1]; for instance, they serve as catalysts for many types of organic reactions [2–6] and act as magnetoactive [7,8] and optical [9] materials. Manganese complexes are of special interest because of their potential activity in small molecule activation [10].

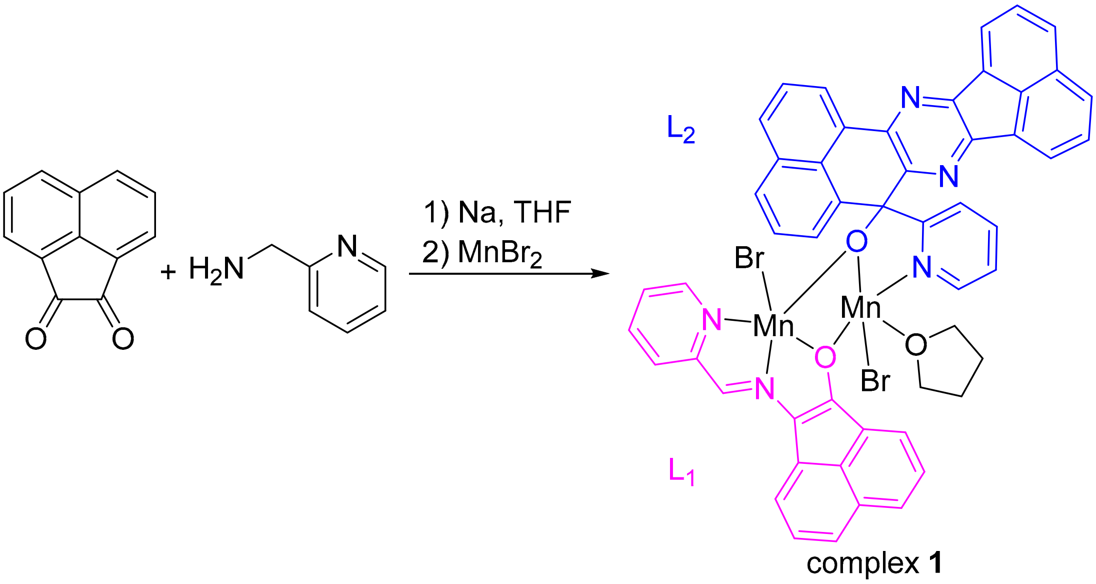
The synthesis of alkyl-BIANs is often complicated by side reactions occurring between alkyl-substituted primary amines and acenaphthenequinone (AQ) [11–16]. This is the reason for a limited number of known, well-characterized alkyl-BIANs. Sometimes, the reaction of primary alkyl amine with AQ leads to a large number of by-products, whereas the desired product is practically absent. For example, as a result of the reaction of AQ with benzylamine, the authors identified several by-products, as shown in Scheme 1 [11–16]. This behavior can be explained by a set of isomerization/tautomerization, oxidation, and hydrolysis reactions during the treatment of primary aliphatic amine and AQ.



Scheme 1. Possible by-products of the reaction between aliphatic amine and AQ according to the literature.

2. Results

In this work, we performed an *in situ* condensation reaction between 2-picolylamine and AQ. Our efforts to purify the reaction mixture by column chromatography failed because of air sensitivity and the formation of an insoluble resinous precipitate. Therefore, we carried out an *in situ* chemical reduction of the crude reaction mixture obtained in the previous step by metallic sodium (1.1 equiv. per 1 mol of initial AQ) in an inert nitrogen atmosphere. After sodium was fully dissolved, manganese(II) bromide was added. The resulting product was crystallized to give manganese complex **1**. Isolated complex **1** demonstrated EPR silence at room temperature. The ^{1}H NMR spectrum of complex **1** was also not informative because of the broadening of proton signals (see Supplementary Materials). We managed to describe the molecular structure of **1** by single-crystal X-ray diffraction. Thus, it was found that neutral binuclear complex **1** contained not only the target mono-iminoacenaphthene ligand (L_1) but also an unexpected 14-(pyridin-2-yl)-14*H*-acenaphtho[1,2-*b*]naphtho[1,8-*fg*]quinoxalin-14-ol ligand (L_2). The overall reaction scheme and structural formula of the final product are shown in Scheme 2.



Scheme 2. Synthesis of binuclear manganese complex **1**.

Complex **1** crystallized in the triclinic space group $P\overline{1}$ with tetrahydrofuran (THF) solvent molecules. According to X-ray diffraction data, compound **1** was a neutral binuclear complex with the Mn1···Mn2 internuclear distance of 3.2818(7) Å, indicating the absence of metal–metal bonding, as shown in Figure 1. The manganese atoms differed in their coordination geometry, namely, the atom Mn1 adopted distorted square pyramidal coordination with geometry index [17] τ_5 = 0.19, while the atom Mn2 was close to octahedral one if the elongated coordination bond Mn2–N3 of 2.493(3) Å was taken into account. The ligand L_1 was coordinated by Mn1 via the atoms O1, N1, and N2, whereas the ligand L_2 bound Mn2 through the atoms N3, N5, and O2 as well as Mn1 through the oxygen atom O2. Internuclear distances of the coordination sphere are listed in the figure caption. The positions of the hydrogen atoms of **1** were confirmed by Fourier maps and corresponded to the skeletal formula in Scheme 2. The analysis of bond lengths within the ligand L_1 in complex **1** showed the migration of double bond from N1–C102 (1.369(5) Å) to N1–C21 (1.289(5) Å). The charge distribution analysis showed that L_2 was an anion with a formal negative charge of −1 on oxygen atom O2. The ligand L_1 also demonstrated anionic character.

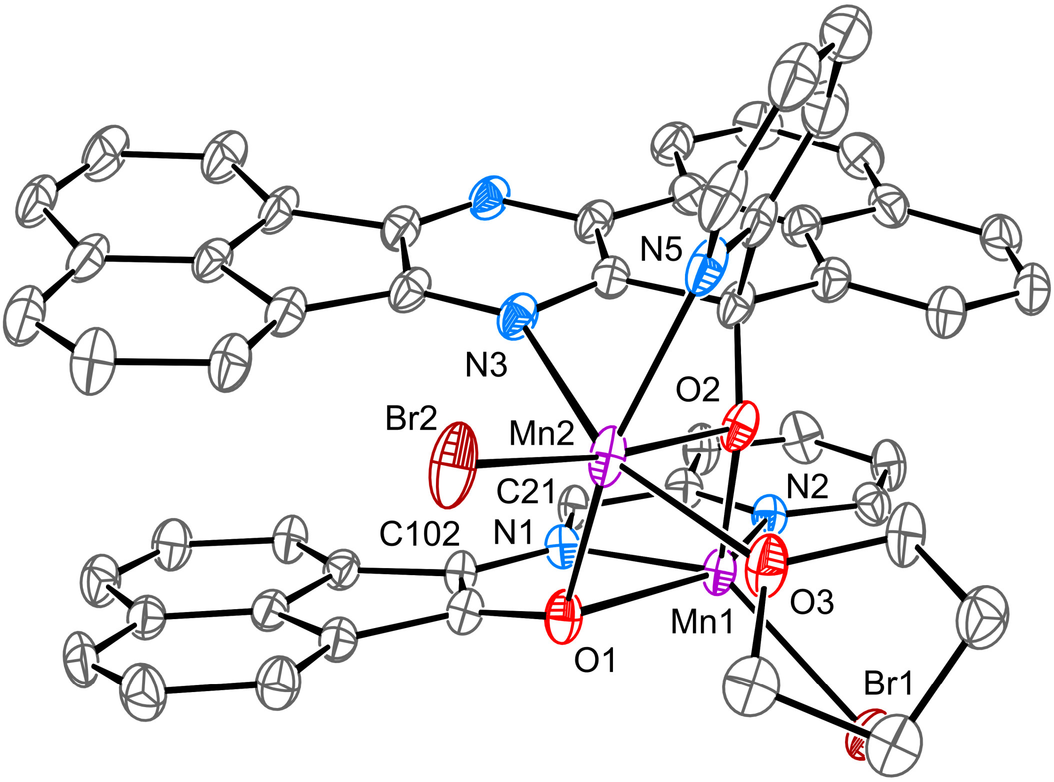


Figure 1. Molecular structure of **1** in the crystal with thermal ellipsoids at the 50% probability level according to single-crystal X-ray diffraction. Hydrogen atoms and solvent molecules are omitted for clarity. Selected interatomic distances [Å]: Br1–Mn1 2.4871(7), Mn1–O1 2.316(3), Mn1–O2 2.031(3), Mn1–N1 2.191(3), Mn1–N2 2.265(3), Br2–Mn2 2.5335(7), Mn2–O1 2.208(3), Mn2–O2 2.139(3), Mn2–O3 2.199(3), Mn2–N3 2.493(3), Mn2–N5 2.264(4).

3. Materials and Methods

Preparation. All manipulations were carried out under nitrogen, using the standard Schlenk technique or in a glove box. The solvents (THF and hexane) were distilled from sodium/benzophenone and stored over 3 Å molecular sieves under nitrogen gas. Acenaphthenequinone (95%, CAS—82-86-0), 2-aminomethyl-pyridine (99%, CAS 3731-51-9), and manganese(II) bromide $MnBr_2$ (98%, CAS 13446-03-2) were purchased and used without preliminary purification.

Synthesis of manganese complex **1**. A solution of 1 equivalent of 2-aminomethyl-pyridine (5 mmol, 0.54 g) in 3 mL of THF was dropwise added to a solution of 1 equivalent of acenaphthenequinone (5 mmol, 0.91 g) in 30 mL of THF. The reaction mixture was stirred at room temperature for about 24 h. Then, metallic sodium (1.1 equiv., 0.0023 g) was added and the solution was stirred for another 24 h. After that, manganese(II) bromide was added in one portion to the reaction mixture and, after 3 h of intense stirring, the solution was filtered. The filtrate was concentrated under a vacuum.

Single-crystal X-ray diffraction. The monocrystal analyzed was obtained by slow diffusion of *n*-hexane in THF at −35 °C. The diffraction data of **1** were registered on a Bruker D8 QUEST diffractometer with a PHOTON III area detector and an IμS DIAMOND microfocus X-ray tube using Mo $K\alpha$ (0.71073 Å) radiation at 105(2) K. The data reduction package *APEX*4 was used for data processing. The data collected were corrected for systematic errors and absorption: empirical absorption correction based on spherical harmonics according to the Laue symmetry $\bar{1}$ using equivalent reflections. The structure was solved by the direct methods using *SHELXT*-2018/2 [18] and refined by the full-matrix least-squares on F^2 using *SHELXL*-2018/3 [19]. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were found by Fourier maps, inserted at the calculated positions, and refined as riding atoms.

Crystallographic data for **1**. $C_{58}H_{47}Br_2Mn_2N_5O_{4\cdot 5}$, plate (0.098 × 0.012 × 0.007 mm^3), formula weight 1155.70 g mol^{-1}; triclinic, $P\overline{1}$ (No. 2), a = 11.4754(3) Å, b = 13.0017(4) Å, c = 16.9515(5) Å, α = 90.9576(10)°, β = 103.9529(10)°, γ = 90.4510(11)°, V = 2454.01(12) Å^3, Z = 2, Z' = 1, T = 105(2) K, d_{calc} = 1.564 g cm^{-3}, μ(Mo $K\alpha$) = 2.199 mm^{-1}, F(000) = 1172; $T_{max/min}$ = 0.9281/0.8469; 64665 reflections were collected (1.945° $\leq \theta \leq$ 25.349°, index ranges: $-13 \leq h \leq 13$, $-15 \leq k \leq 15$, and $-20 \leq l \leq 20$), 8993 of which were unique, R_{int} = 0.0749, R_σ = 0.0455; completeness to θ of 25.349° 100.0%. The refinement of 713 parameters with 324 restraints converged to $R1$ = 0.0430 and $wR2$ = 0.1065 for 6802 reflections with $I > 2\sigma(I)$ and $R1$ = 0.0636 and $wR2$ = 0.1180 for all data with goodness-of-fit S = 1.057 and residual electron density $\rho_{max/min}$ = 1.091 and −0.565 e Å^{-3}, rms 0.091; max shift/e.s.d. in the last cycle 0.001.

Deposition number CCDC 2244472 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures (accessed on 24 February 2023).

4. Conclusions

Thus, a new binuclear manganese complex with two different N,O-ligands was obtained and structurally characterized by single-crystal X-ray diffraction. An interesting ligand environment near two manganese centers possibly makes this complex promising for further application in small molecule activation reactions.

Supplementary Materials: The following supporting information can be downloaded: EPR spectrum, ^{1}H NMR spectrum, and crystallographic data in Crystallographic Information File (CIF) format.

Author Contributions: V.V.K., conceptualization, investigation, writing—original draft preparation; R.R.F., conceptualization, formal analysis, investigation, writing—original draft preparation, visualization, data curation; Y.H.B., writing—review and editing, supervision. All authors discussed and approved the final version. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Data are contained within the article and the Supplementary Materials.

Conflicts of Interest: The authors declare no conflict of interest.

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