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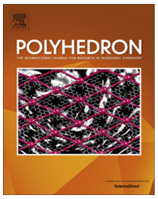

Mn(II) and Zn(II) ions catalytic oxidation of o-phenylenediamine and characterization, X-ray crystal structure and solution study of the final products $DAPH^+Cl^-\cdot 3H_2O$ and $[DAPH][Zn(dipicH)(dipic)]\cdot 4H_2O$

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ABSTRACT

Compound $DAPH^+Cl^-\cdot 3H_2O$ (**1**), and complexes $Mn(dipic)(H_2O)_3$ (**2**) and $[DAPH][Zn(dipicH)(dipic)]\cdot 4H_2O$ (**3**), ($dipicH_2$ = 2,6-pyridinedicarboxylic acid and DAP = 2,3-diaminophenazine) were prepared from the reaction of $MgCl_2\cdot 4H_2O$ and $ZnCl_2$ with mixture of o-phenylenediamine (OPD) and 2,6-pyridinedicarboxylic acid in water. These compounds were characterized by elemental analysis, FTIR, ^1H NMR and UV–Vis spectroscopy. The solid-state structure of $[DAPH][Zn(dipicH)(dipic)]\cdot 4H_2O$ (monoclinic, $P2_1/c$) was determined by the single crystal X-ray diffraction method. The protonation constants of dipic and DAP, in all of probability protonated forms, the equilibrium constants for the dipic–DAP proton transfer system and the stoichiometry and stability constants of binary and ternary complexes of this system with Zn^{2+} and Mn^{2+} ions in aqueous solution were investigated by the potentiometric pH titration method. The stoichiometries of the most complex species in solution were compared with corresponding crystalline complexes in the solid state.

1. Introduction

Phenylenediamines (known as Benzenediamines) are aromatic amines with two amino groups attached to benzene. They are found in ortho, meta and para isomeric forms. The ortho form (OPD) of phenylenediamine has two amino groups at the one and two positions of the benzene ring. o-Phenylenediamine in addition to acting as monodentate [1], chelating bidentate [2] and bridging [3] ligand, plays an important role in the synthesis of other functional diamines, such as 2,3-diaminophenazine (DAP) [4].

2,3-Diaminophenazine (DAP) is a heterocyclic aromatic diamine, which has been the subject of interest to both chemists and biochemists because of its chemical and physical properties [5]. DAP can coordinate with the metal center as a chelating bidentate ligand [6], and it can be also found in some complexes as a discrete cation [7].

Synthetically, DAP is prepared by the catalyzed autosensitized or photochemical oxidation cyclization of o-phenylenediamine (OPD). Perhaps the first evidence from the oxidation of OPD molecules by ferric chloride and ring-forming dimerization came from Griess [8]. The oxidation by various oxidants, including, silver oxide, lead(IV) oxide, cupric chloride, cupric nitrate, cupric hydroxide, cupric acetate and perchlorate and by cobalt perchlorate has been also reported in literature [5,7,9–13]. Three years ago, Mei et al. [13] in an effort to prepare diamine complexes of copper from copper chloride anhydrous reaction with OPD, several structures of hydrochloride salt of this compound with different solvents has been reported. Recently, the aerobic oxidation of o-phenylenediamine to 2,3-diaminophenazine in the present of copper(II) complexes as catalyst is also reported [14].

2,6-Pyridinedicarboxylic acid (dipicolinic acid, $dipicH_2$), is a versatile ligand with the ability to act as a bidentate, tridentate, and/or bridging ligand [15–19]. It can interact with metal ions in dianionic ($dipic^{2-}$), monoanionic ($dipicH^-$) or neutral ($dipicH_2$) forms [20,21]. A large number of octahedral complexes containing dipicolinic as a tridentate ligand with the first row transition metal ions such as Mn^{2+} or Zn^{2+} ions have been reported [22–33]. In these complexes, a single planar dipic ligand binds to metal centers by tridentate (O,N,O′) chelation and other ligands such as H_2O or pyridine based heterocyclic occupy the remaining three sites, thereby

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Table 1
Crystal data, data collection and structure refinement details for [DAPH][Zn(dipicH)(dipic)]·$4H_2O$.

Empirical formula	$C_{26}H_{26}N_6O_{12}Zn1$
Molecular weight	679.92
Color	dark pink
T (K)	293
λ (Å)	CuK$_\alpha$ (1.5418 Å)
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	8.9710(5)
b (Å)	19.4740(8)
c (Å)	17.6010(7)
α (°)	90
β (°)	115.874(6)
γ (°)	90
V (Å^3)	2766.7(3)
Z	4
D_{calc} (g cm^{-3})	1.632
θ rang for data collection (°)	3.5943–70.7825
Index range	$-6 \leqslant h \leqslant 10$, $-20 \leqslant k \leqslant 23$, $-21 \leqslant l \leqslant 18$
Absorption coefficient (mm^{-1})	1.927
$F(000)$	1400
Reflections collected	10796
Independent reflections	5168 [$R_{int} = 0.0902$]
Parameters	440
Goodness-of-fit (GOF) on F^2	0.961
R_1 [$I > 2\sigma(I)$]	0.0442
wR_2 (all data)	0.0902
Largest ΔF peak and hole (e Å^{-3})	0.204 and −0.288

forming a distorted octahedral coordination geometry [22–25], or two planar dipic molecules coordinate perpendicularly generating a distorted octahedral coordination geometry [26–33].

As part of our studies of the complexes containing 2,6-pyridinedicarboxylic acid and o-phenylenediamine or 2,3-diaminophenazine, we have recently reported the synthesis, characterization, crystal structures and solution study of new complexes $[OPDH]_2[Co(dipic)_2]\cdot H_2O$ [34] and $[DAPH][H_3O][Cu(dipic)_2]\cdot 3H_2O$ [7].

In this work, we report the synthesis, crystal structure and solution study of compounds $DAPH^+Cl^-\cdot 3H_2O$ and $Mn(dipic)(H_2O)_3$ and complex anion $[Zn(dipic)(Hdipic)]^-$ containing the 2,3-diaminophenazinium as cation namely [DAPH] $[Zn(dipic)(Hdipic)]^-\cdot 4H_2O$.

2. Experimental

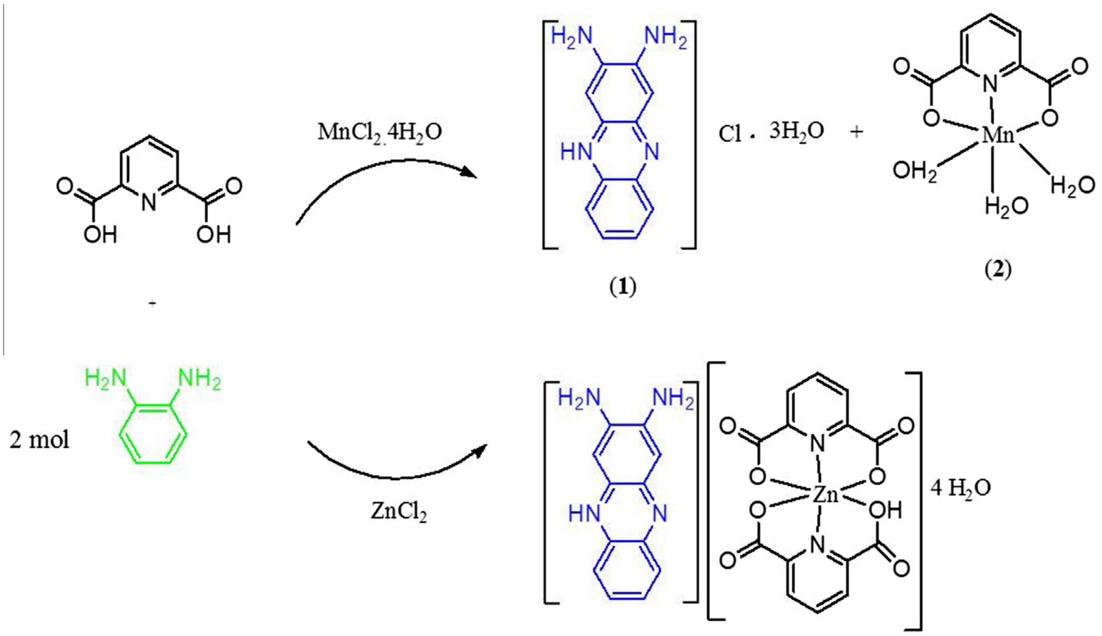
2.1. Materials and methods

2,6-Pyridinedicarboxylic acid (dipicH$_2$), o-phenylenediamine (OPD), $MgCl_2\cdot 4H_2O$ and $ZnCl_2$ were obtained from Merck. Elemental analyses were performed by using a Leco, CHNS-932 elemental analyzer. Fourier transform infrared spectra were recorded on a FT-IR JASCO 680-PLUS spectrometer in the region of 4000–400 cm^{-1} using KBr pellets. Melting points were determined with an Electrothermal IA-900 apparatus. ^1H NMR spectra were obtained on a Bruker 300 spectrometer. Chemical shifts were reported on the δ scale relative to TMS. Electronic spectra were obtained using a UV-JASCO-570 spectrometer

2.2. Synthesis

2.2.1. Isolation of $DAPH^+Cl^-\cdot 3H_2O$ (**1**) and $Mn(dipic)(H_2O)_3$ (**2**)

These compounds have been reported previously in different methods [10,25]. Solution of 2,6-pyridinedicarboxylic acid (1 mmol, 0.167 g) was refluxed with o-phenylenediamine (2 mmol, 0.216 g) for 1 h then a solution of $MgCl_2\cdot 4H_2O$ (1 mmol, 0.197 g) was added drop wise to the reaction mixture, which produced white precipitate quickly. The obtained precipitate was filtered off, washed with water and dried in air. The yield was 67%. *Anal.* Calc. for $C_7H_9MnNO_7$ (MW = 274.09): C, 30.67; H, 3.31; N, 5.11. Found: C, 30.79; H, 3.25; N, 5.51%. FT-IR (as KBr disks, cm^{-1}): 3400, 2923, 1610, 1591, 1570, 1441, 1395, 1016, 721. UV–Vis



(3)

Scheme 1. Synthetic route to the synthesis of (1), (2) and (3).