Vapochromism and Magnetochemical Switching of a Nickel(II) Paddlewheel Complex by Reversible NH₃ Uptake and Release

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Abstract: Reaction of [NiCl₂(PnH)]₄ (1) (PnH = 6-tert-butyl-pyridazine-3-thione) with NiCl₂ affords the binuclear paddlewheel (PW) complex [Ni₂(Pn)₄] (2). Diamagnetic complex 2 is the first example of a PW complex capable of reversibly binding and releasing NH₃. The NH₃ ligand in [Ni₂(Pn)₂(NH₃)₂] (2-NH₃) enforces major spectroscopic and magnetic susceptibility changes, thus displaying vapochromic properties (λ_max(2) = 532 nm, λ_max(2-NH₃) = 518 nm) and magnetochemical switching (S = 0; 2-NH₃: S = 1). Upon repeated adsorption/desorption cycles of NH₃ the PW core remains intact. Compound 2 can be embedded into thin polyurethane films (°) under retention of its sensing abilities. Therefore, 2 qualifies as reversible optical probe for ammonia. The magnetochemical switching of 2 and 2-NH₃ was studied in detail by SQUID measurements showing that in 2-NH₃ solely the Ni atom coordinated the NH₃ molecule is responsible for the paramagnetic behavior.

Introduction

The paddlewheel (PW) motif with four bridging ligands spanning two metal centers of the general formula [Mₓ(XY)₄], (X,Y = O, N, P, S, C) is among the most studied metal connectors in coordination chemistry.[1] Recently, we have begun to study the relatively unexplored chemistry of the S,N-bidentate ligand 6-tert-butyl-pyridazine-3-thione (PnH).[2] Comparatively few structurally characterized divalent group 10 PWs have been published (Pt ≈ 100, Pd, Ni < 15 each). Reported Ni₃-PWs are either symmetrically bridged by O,O- [3] S,S-[4,5] or N,N-[6-9] type ligands or asymmetrically bridged by S,O-[10] or S,N-bridging ligands (Scheme 1).[11,12] In principle four different isomers are possible for an asymmetric ligand system like PnH (Figure S4).

The remarkable magnetic properties of PW complexes have been previously described in literature. If metal-metal bonds are absent, divalent group 10 PWs are expected to be diamagnetic because of the square-planar ligand field around the two metal sites.[13] PdⅡ and PtⅡ PWs have been shown to strictly maintain their essentially square-planar geometry around the metal centers. NiⅡ-PWs on the other hand have been reported to be mainly paramagnetic (some exceptions are known[13]), because of additionally coordinated axial ligands at one or both metal sites.[6-9,11,12] The binding of an axial ligand changes the coordination sphere at the metal site to square-pyramidal thus rendering such PW complexes paramagnetic. A search in the Cambridge Structural Database revealed that in O,O-, S,O- and S,S-bridged NiⅡ-PWs, the [NiO₄] sites are always coordinated by an axial ligand, while the [Ni₂S₄] sites are not.[14] S,N-Bridged NiⅡ-PWs have been reported either with[11] or without[10,13] axially bound donor ligands. To the best of our knowledge, in none of those both situations have been realized within a given paddlewheel. However, this would be highly interesting as it offers the possibility for molecular, magnetic switching triggered by...
a donor ligand. Such a magnetic bistability has so far been mostly observed in tailored solid state materials, where cooperative effects (e.g. magnetic coupling or lattice interactions) of a large number of magnetic centers may cause a hysteresis between two spin states.\textsuperscript{[16]} The limited control over structural parameters, as well as crystal lattice or long-range order breakdowns, together with a sometimes unfavorable low temperature window of hysteresis, remain drawbacks for such solid state materials.\textsuperscript{[17,18]} In contrast comparatively few examples of molecules in solution showing magnetic bistability devoid of cooperative effects have been disclosed.\textsuperscript{[18–21]} An interesting example of a fully reversible magnetocoupled switching molecule was reported some years ago where a Ni\textsuperscript{III} porphyrin complex with a tethered azo-pyridine linker can adopt two magnetic states depending on light.\textsuperscript{[20]} Irradiation causes isomerization within the azo-group where the cis-configuration allows the pyridine moiety to coordinate to the Ni\textsuperscript{III} center, thereby inducing the magnetocoupled switching. Furthermore, magnetic bistability was recently reported for a mononuclear, square planar Ni\textsuperscript{III}-complex in the solid state, in which reversible axial coordination of methanol vapors triggered magnetocoupled switching.\textsuperscript{[21]} Additionally, the complex displayed highly methanol-selective vapochromism for the two different spin states.

Here, the synthesis of complex \([\text{Ni}_{3}(\text{Pn})]_2\) (2) is reported, which represents the first example of a Ni\textsubscript{II}-PW complex capable of reversibly binding NH\textsubscript{3} both in the solid state and in solution. The coordination of NH\textsubscript{3} is accompanied by a change of color (dark brown 2 to brown-red 2NH\textsubscript{3}, Figure 2) and magnetism (switching from diamagnetic 2 to paramagnetic 2NH\textsubscript{3}, Figure 3). The reversibility of the observed switching qualifies 2 as a potential probe for ammonia detection.\textsuperscript{[22]} The sensing ability of 2 is also realized when coated in thin polyurethane films (Hydromed D4, vide infra).

**Results and Discussion**

Complex 2 is accessible by a step-wise assembly via mononuclear Ni\textsuperscript{II} precursor \([\text{NiCl}_2(\text{PnH})]_2\) (1) (Scheme 1). In-situ deprotonation of 1 with a base (e.g. NaH, NEt\textsubscript{3}) in ethanol or acetonitrile and subsequent addition of one equivalent of NiCl\textsubscript{2} yielded diamagnetic PW complex 2 in analytically pure form as a microcrystalline dark brown solid. The crystalline material consists of an isomeric mix of (2,2)-, (3,1)- and (4,0)-isomers (Figure S4), as observed by \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopy (Figure S1 and S2). When aqueous NH\textsubscript{3} was used as base, a dark red-brown solid was obtained which could be identified as the paramagnetic Ni\textsubscript{II}-PW complex \([\text{Ni}_3(\text{Pn})]_2 \cdot \text{NH}_3\) (2NH\textsubscript{3}). The \textsuperscript{1}H NMR spectrum of 2NH\textsubscript{3} shows broad, downfield shifted signals due to its paramagnetism. Magnetic susceptibility measurements with a Gouy balance \((\mu_{\text{eff}} = 2.85)\) revealed two unpaired electrons (Table S1). We therefore conclude that upon exposure to NH\textsubscript{3} a full isomerization to the (4,0)-isomer occurs, finally giving 2NH\textsubscript{3}.

Single-crystal X-ray diffraction analysis allowed unambiguous determination of the molecular structures of the Ni\textsubscript{II}-PW 2 and 2-NH\textsubscript{3} (Figure 1).\textsuperscript{[24]} In the solid state 2 and 2-NH\textsubscript{3} show the well-established PW core.

The Ni atoms in 2 are located in close proximity to each other (Ni-Ni 2.4626(5) Å), corresponding to the shortest Ni--Ni distance reported for S,N-bridged Ni\textsubscript{II}-PWs. Previously reported Ni-Ni bond distances are at 2.648(2) Å in [Ni\textsubscript{II}(tzt)]\textsubscript{2} (tzt = thiazoline-2-thione)\textsuperscript{[11]} and 2.574(2) Å in [Ni\textsubscript{II}(mim\textsubscript{III})\textsubscript{2}] (mim\textsubscript{III} = tert-butylimidazol-thione).\textsuperscript{[12]} Coordination of NH\textsubscript{3} to the PW framework results in an elongation of the Ni-Ni distance to 2.5008(2) Å in 2-NH\textsubscript{3}. In the penta-coordinate Ni-Ni-NH\textsubscript{3}-moiety of 2-NH\textsubscript{3} the bound NH\textsubscript{3} has assumed the apical position (Ni-NH\textsubscript{3}: 2.0471(10) Å). Ni-S bonds are significantly shortened and Ni--N bonds elongated compared to 2.

Addition of both, aqueous ammonia to 2 in solution (e.g. in CHCl\textsubscript{3}) or gaseous NH\textsubscript{3} to solid 2, results in immediate formation of 2-NH\textsubscript{3} accompanied by a change of spectral as well as magnetic properties. The apparent color change from dark brown 2 to brown-red 2-NH\textsubscript{3}, Figure 2) and magnetism (switching from diamagnetic 2 to paramagnetic 2-NH\textsubscript{3}, Figure 3). The reversibility of the observed switching qualifies 2 as a potential probe for ammonia detection.\textsuperscript{[22]} The unusual uptake of ammonia from both aqueous and gaseous sources was further investigated with respect to its reversibility. A thermogravimetric analysis (TGA) experiment of 2-NH\textsubscript{3} showed a loss of approx. 3 wt% between 70°C and 120°C, consistent with loss of one NH\textsubscript{3} molecule. Upon further heating, no significant change in weight occurs up to 320°C. Thereafter, a weight loss of 34 wt% was observed indicating thermal decomposition of complex 2. Accordingly, solid 2-NH\textsubscript{3} was found to re-convert to 2 at 110°C under dynamic vacuum within one hour. \textsuperscript{1}H NMR spectroscopy confirms the coordination and release
of NH$_3$ without decomposition of the PW-core (Figure S3). It is interesting to note that the addition of aqueous ammonia to 2 is selective for NH$_3$ over H$_2$O. The addition of water to 2 leads in principle to the analogous aqua complex 2·H$_2$O. However, the coordination seems to be far weaker, as magnetic susceptibility measurements of the isolated materials always showed less than two unpaired electrons, indicating that only mixtures of 2 and 2·H$_2$O were obtained.

The potential of 2 as a molecular probe for NH$_3$ was explored by encapsulation in a suitable hydrogel and subsequent foil formation (2'). Thin foils containing 5, 10 or 20 wt% of 2 were prepared by dissolving the complex and the commercially available polyurethane hydrogel Hydromed D4 in CHCl$_3$ and knife-coating of the resulting solution onto a transparent poly(ethylene terephthalate) support to give a sensing film of about 7.5 µm in thickness. The foils are stable in water with no noticeable leaching of 2 and are permeable to NH$_3$. Similar to bulk 2, the 2' foils react with NH$_3$ vapors forming 2·NH$_3$ under color change. Also dipping the foil into aqueous NH$_3$ solutions (concentration range from 19.6 to 0.03 M NH$_3$) caused immediate color change (Figure 2, right).

The foils are thin enough to be directly measured in a quartz cuvette in the UV/Vis photometer. In order to test the stability of 2' under repeated NH$_3$ exposure and removal, the foils were dipped in an aqueous NH$_3$ (35%) solution (changing color to brown-red). In contrast to 2·NH$_3$, which is completely insoluble in H$_2$O, the NH$_3$ in 2·NH$_3$ can be easily removed by soaking the foil for 20 min in 200 mL of deionized H$_2$O (changing color back to dark brown). After each cycle a UV/Vis spectrum was acquired and compared to pristine 2' proving that at least nine cycles of NH$_3$ coordination and removal are possible without apparent decomposition of 2' (Figure S5).

In order to further probe the magnetic properties of 2 and 2·NH$_3$, the complexes were investigated by SQUID magnetometry. Magnetic susceptibility data was collected in dichloromethane in the temperature range from 300 to 2.7 K at a magnetic field of 70000 Oe. The CH$_2$Cl$_2$-solvent is frozen below 176 K and contributes to a sizeable temperature-independent diamagnetic background for $T < 173$ K, which has to be carefully subtracted from the total magnetic signal. The utmost sensitivity of the SQUID magnetometer allows a correct determination of the magnetic behavior in switching from the diamagnetic sample 2 (Figure 3b) to paramagnetic 2·NH$_3$, by up-scaling the observed paramagnetic signal to the molar susceptibility $\chi M$ (Figure 3b). A high magnetic field of 70000 Oe was applied to saturate the sample with its characteristic turn-down of $\chi M$ at low temperatures ($< 20$ K; Figure 3b). In contrast, the diamagnetism remains constant (level set to zero). The influence of a ligand field (D) has been included in the simulation. The approach to the limiting value of 1 cm$^3$K mol$^{-1}$ proves that the bi-nuclear Ni-complex 2·NH$_3$ consists of only one paramagnetic Ni-atom ($S = 1$) near the NH$_3$-site, exposed to a weak ligand field of $D = 15$ cm$^{-1}$, the other Ni-atom remains diamagnetic.[3] No evidence for a Ni-Ni bond could be observed. For 2 both Ni-atoms reside in a square planar surrounding with vanishing spin ($S = 0$), thus being diamagnetic and independent on temperature (Figure 3b). In the simulation the randomness of all spatial paddlewheel orientations with respect to the magnetic field has been considered.

**Conclusion**

In conclusion, we succeeded in synthesizing a novel Ni$_2$-PW complex (2) with interesting vapochromic properties and magnetoochemical switching of spin states upon exposure to aqueous or gaseous ammonia. The reaction of diamagnetic [Ni$_3$(P$_{10}$)$_2$] (2) to paramagnetic [Ni$_3$(P$_{10}$)(NH$_3$)$_2$] (2·NH$_3$) is the first report of a reversible, magnetically tunable PW system, that features NH$_3$ uptake and release under mild reaction conditions without a collapse of the PW core. Both 2 and 2·NH$_3$ are fully characterized including single crystal X-ray diffraction analysis and SQUID magnetometry. Furthermore, 2 can be easily incorporated into thin polyurethane foils (2') under complete retention of its reversible NH$_3$ sensing capabilities.

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**Conflict of interest**

The authors declare no conflict of interest.

**Stichwörter:** ammonia · nickel complexes · paddlewheel complexes · spin-state switching · vapochromism
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