



Chromogenic behaviour of a family of hydrazine and hydrazone metal complexes



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ARTICLE INFO

Article history:

Received 23 October 2014

Received in revised form 20 December 2014

Accepted 5 January 2015

Available online 12 January 2015

Keywords:

Chromogenic behaviour

Hydrazone

Metal complex

UV–Vis spectroscopy

ABSTRACT

A family of five tridentate hydrazone-based ligands with an *N,N,N*-, *N,N,O*- or *N,N,S*-donor environment is reported. The tridentate ligands are derived from either 2-(1-methylhydrazinyl)pyridine or 2-hydrazinylpyridine and have been obtained by condensation with a series of aldehydes and ketones carrying one potential metal-binding site. To study their metal complexation behaviour, the five ligands and one of the bidentate precursor compounds have been reacted with ten different transition and main group metal ions. An interesting chromogenic behaviour has been found: ligands **1**, **3** and **H6** (with an *N,N*-, *N,N,N*- and *N,N,O*-donor environment) give very specific colour changes in the presence of Fe^{2+} , whereas ligand **H7** specifically forms a dark brown coloured complex with Co^{2+} only. All ligands form yellow to orange complexes with Pd^{2+} . Three of these metal complexes were characterized by single-crystal X-ray diffraction analysis: the molecular structures of $[\text{Pd}(\mathbf{1})\text{Cl}_2]$, $[\text{Cu}(\mathbf{1})\text{Cl}_2]_2$, and $[\text{Cu}(\mathbf{6})\text{Cl}]$ give an insight into the metal-binding behaviour of the ligands and nicely confirm the bidentate binding of ligand **1** and the tridentate binding of the deprotonated ligand **6**[−]. It is proposed that the chromogenic behaviour of the ligands can be useful for the development of selective metal ion sensors.

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1. Introduction

Since Emil Fischer established the use of hydrazones in chemistry in 1884, a wide range of applications has been reported [1]. The Wolff–Kishner reduction or *aza-Nenitzescu* indole cyclisation are examples for the importance of hydrazones in chemical synthesis [2,3]. Further examples for an application of these Schiff base-type compounds include their use as antimicrobial agents or in the field of molecular recognition, e.g., in self-assembling nanoclusters or as selective sensors [4–6]. Because of their well-known affinity towards metal ions, we recently reported the use of hydrazone ligands as potential artificial nucleobases for metal-mediated base pairs, i.e., in the context of enabling the site-specific introduction of metal-based functionality into artificial DNA double helices [7]. In the past few years, hydrazone-based motifs also gained importance as chromogenic agents for the specific detection of transition metals with the naked eye or by UV–Vis spectroscopy, respectively [8,9]. Hence, we set out to investigate the chromogenic behaviour of our series of bi- and tridentate hydrazine- and hydrazone-based ligands in the presence of various metal ions (Cr^{3+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Pd^{2+} , Cu^{2+} , Zn^{2+} , Hg^{2+} and Al^{3+}).

2. Experimental

2.1. Measurements

Mass spectra were recorded on a Bruker Daltonics Micro TOF spectrometer with the electron ionisation (EI) or electrospray ionisation (ESI) method. The elemental analyses were recorded on a Vario EL III CHNS analyser. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance (I) 400 and Avance (III) 400 spectrometers with an internal standard relative to TMS ($\delta = 0$ ppm) for measurements in CDCl_3 . In case of $\text{DMSO}-d_6$ and $\text{D}_2\text{O}/\text{DMSO}-d_6$ mixtures, the residual solvent peak was used as internal standard. The UV–Vis spectra were recorded on a Varian Cary 100 Bio spectrometer. The data were collected from 800 nm to 200 nm with a data interval of 1 nm and a scan rate of 600 nm min^{-1} at 15°C in methanol. A manual baseline correction was applied. IR spectra were recorded on a Bruker Vector 22 IR spectrometer. Single-crystal X-ray diffraction data were collected with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) on a Bruker Quazar diffractometer ($[\text{Pd}(\mathbf{1})\text{Cl}_2]$), Bruker D8 Venture diffractometer ($[\text{Cu}(\mathbf{1})\text{Cl}_2]_2$) and a Stoe Stadivari diffractometer ($[\text{Cu}(\mathbf{6})\text{Cl}]$). The structures were solved by direct methods and were refined by full-matrix, least squares on F^2 by using the SHELXTL and SHELXL-97 programs [10]. Relevant crystallographic data are listed in Table 1.

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2.2. Ligands and complexes

The synthesis of the hydrazone-based compounds **3–5** has been reported previously [7]. Compounds **H6** and **H7** have been synthesized analogously. In the key step of this synthesis, a solution of compound **1** (or **2**) [11] in ethanol was treated with an equimolar amount of the respective aldehyde (ketone) and acetic acid as a catalyst. The reaction mixture was stirred for 1 h at 58 °C. The reaction volume was reduced to the half, water was added and the respective product crystallized at –26 °C overnight. Filtration and drying at 40 °C led to the respective clean product in 54–74% yield. Non-methylated analogues of **H6** and **H7** have been reported previously by other groups and are not subject of this study [12,13].

Metal complexes were obtained by the addition of a methanolic solution of the respective ligand to a methanolic solution of an equimolar amount of metal salt or precursor complex (Co(NO₃)₂·6H₂O, Cr(NO₃)₃·9H₂O, CuCl₂·2H₂O, FeSO₄, MnCl₂·4H₂O, [PdCl₂(cod)], NiCl₂·6H₂O, CuI, NiSO₄·6H₂O, ZnCl₂). Stirring for 1–3 h at ambient temperature led to the product as an amorphous solid, which was purified by filtration and washing with a methanol/Et₂O mixture. The respective pure product was isolated after drying at 40 °C overnight in 70–92% yield. During the investigation of the chromogenic behaviour, Pd(OAc)₂ in CH₃CN was used instead of [PdCl₂(cod)] because of better solubility.

Ligand H6: ¹H NMR (CDCl₃): δ = 11.39 (s, 1H, OH), 8.25 (dd, 1H, H6'), 7.78 (s, 1H, CH=N), 7.58 (dd, 1H, H3''), 7.30 (dd, 1H, H4'), 6.91–6.85 (m, 3H, H4'', H3', H5''), 6.82 (dd, 1H, H5'), 3.93 (s, 3H, OCH₃), 3.68 (s, 3H, NCH₃) ppm. ¹³C NMR (CDCl₃): δ = 156.5 (C2'), 148.2 (C2''), 147.3 (C6'), 146.3 (C6''), 138.1 (C3''), 137.7 (CH=N), 121.6 (C4''), 119.4 (C1''), 119.0 (C5''), 116.2 (C5'), 111.9 (C3'), 108.6 (C4'), 56.0 (OCH₃), 29.1 (NCH₃) ppm. C₁₄H₁₅N₃O₂: C 65.4 (calcd. 65.4), H 5.8 (calcd. 5.9), N 16.4 (calcd. 16.3)%. ESI-MS: *m/z* = 258.1236 ([M+H]⁺ = 258.1243). IR (KBr): $\tilde{\nu}$ (C=N) 1589 (vs) cm⁻¹.

Ligand H7: ¹H NMR (CDCl₃): δ = 9.01 (s, 1H, NH), 8.20 (ddd, 1H, H6'), 7.59 (s, 1H, CH=N), 7.55 (m, 2H, H5', H4'), 6.86 (dd, 1H, H5''), 6.73 (ddd, 1H, H3'), 6.38 (ddd, 1H, H3''), 6.26 (dd, 1H, H4''), 3.62 (s, 3H, CH₃) ppm. ¹³C NMR (CDCl₃): δ = 157.6 (C2'), 147.0 (C6'), 137.3 (C2''), 129.7 (CH=N), 127.0 (C4'), 119.6 (C5''), 114.9 (C3''), 110.6 (C5'), 109.7 (C4''), 109.3 (C3'), 29.4 (CH₃) ppm. C₁₁H₁₂N₄: C 65.6

(calcd. 66.0), H 5.8 (calcd. 6.0), N 27.9 (28.0)%. ESI-MS: *m/z* = 201.1136 ([M+H]⁺ = 201.1140). IR (KBr): $\tilde{\nu}$ (C=N) 1598 (vs) cm⁻¹.

Complex [Pd(1)Cl₂]: ¹H NMR (DMSO-*d*₆): δ = 8.67 (s, 2H, NH₂), 8.31 (dd, 1H, H4), 7.82 (m, 1H, H6), 6.83 (dd, 1H, H5), 6.78 (d, 1H, H3), 3.14 (s, 3H, CH₃) ppm. ¹³C NMR (DMSO-*d*₆): δ = 160.2 (C2), 145.6 (C4), 140.5 (C6), 114.0 (C5), 107.8 (C3), 38.0 (CH₃) ppm. C₆H₉Cl₂N₃Pd·0.25CH₃OH: C 24.6 (calcd. 24.3), H 3.3 (calcd. 3.3), N 13.9 (calcd. 13.6)%. ESI-MS: *m/z* = 228.9825 ([M–2Cl]⁺: 228.9831).

Complex [Pd(1)₂]Cl₂·3H₂O: ¹H NMR (D₂O/DMSO-*d*₆): δ = 8.05 (dd, 2H, H4), 7.72 (d, 2H, H6), 7.04 (dd, 2H, H5), 6.98 (d, 2H, H3), 3.48 (s, 6H, CH₃) ppm. ¹³C NMR (D₂O/DMSO-*d*₆): δ = 162.0 (C2), 147.9 (C4), 143.6 (C6), 117.1 (C5), 110.3 (C3), 39.9 (CH₃). C₁₂H₂₄Cl₂N₆O₃Pd: C 30.6 (calcd. 30.2), H 4.7 (calcd. 5.1), N 17.7 (calcd. 17.6)%. ESI-MS: *m/z* = 176.0305 ([Pd(1)₂]²⁺: 176.0314).

Complex [Cu(1)Cl₂]: C₆H₉Cl₂CuN₃: C 28.0 (calcd. 28.0), H 3.4 (calcd. 3.5), N 16.2 (calcd. 16.3)%. ESI-MS: *m/z* = 220.9774 ([M–Cl]⁺: 220.9781).

Complex [Cu(3)Cl₂]: C₁₂H₁₂Cl₂CuN₄: C 41.5 (calcd. 41.6), H 3.4 (calcd. 3.5), N 16.2 (calcd. 16.2)%. ESI-MS: *m/z* = 310.0040 ([M–Cl]⁺: 310.0047). IR (KBr): $\tilde{\nu}$ (C=N) 1621 (vs) cm⁻¹.

Complex [Mn(3)Cl₂(OH₂)]: C₁₂H₁₄Cl₂MnN₄O: C 40.9 (calcd. 40.5), H 3.8 (calcd. 4.0), N 15.9 (calcd. 15.7)%. ESI-MS: *m/z* = 354.9920 ([M]⁺: 354.9925). IR (KBr): $\tilde{\nu}$ (C=N) 1615 (vs) cm⁻¹.

Complex [Zn(3)Cl₂]: ¹H NMR (DMSO-*d*₆): δ = 11.78 (s, 1H, NH), 8.67 (m, 1H, H4'), 8.19 (m, 2H, H6'', H4''), 8.06 (d, 1H, H6'), 7.92 (dd, 1H, H5''), 7.73 (m, 1H, H3'), 7.16 (m, 2H, H5', H3''), 2.59 (s, 3H, CH₃) ppm. ¹³C NMR (DMSO-*d*₆): δ = 162.9 (C2''), 152.1 (C2'), 145.7 (C4'), 142.0 (C4''), 135.5 (C6', C6''), 115.3 (H₃CC=N), 52.4 (C3'', C5''), 31.2 (C5'), 25.0 (C3'), 4.9 (CH₃) ppm. C₁₂H₁₂Cl₂N₄Zn·0.5H₂O: C 40.4 (calcd. 40.3), H 3.3 (calcd. 3.7), N 15.7 (calcd. 15.7)%. ESI-MS: *m/z* = 311.0037 ([M–Cl]⁺: 311.0042). IR (KBr): $\tilde{\nu}$ (C=N) 1599 (vs) cm⁻¹.

Complex [Cu(4)Cl₂]: C₁₁H₁₁Cl₂CuN₃O·0.33H₂O: C 38.8 (calcd. 38.7), H 3.2 (calcd. 3.4), N 12.3 (calcd. 12.3)%. ESI-MS: *m/z* = 298.9880 ([M–Cl]⁺: 298.9887). IR (KBr): $\tilde{\nu}$ (C=N) 1612 (vs) cm⁻¹.

Complex [Pd(4)Cl₂]: ¹H NMR (DMSO-*d*₆): δ = 8.56 (d, 1H, H6'), 8.37 (s, 1H, CH=N), 8.29 (m, 1H, H4'), 8.11 (dd, 1H, H5'),

Table 1

Crystallographic data for compounds [Pd(1)Cl₂], [Cu(1)Cl₂]₂, and [Cu(6)Cl].

	[Pd(1)Cl ₂]	[Cu(1)Cl ₂] ₂	[Cu(6)Cl]
Empirical formula	C ₆ H ₉ Cl ₂ N ₃ Pd	C ₁₂ H ₁₈ Cl ₄ Cu ₂ N ₆	C ₁₄ H ₁₄ ClCuN ₃ O ₂
Formula weight	300.46	515.20	355.27
Crystal system	monoclinic	triclinic	monoclinic
Space group	C2/c	P $\bar{1}$	P2 ₁ /n
<i>a</i> (Å)	16.175(1)	6.456(5)	6.636(1)
<i>b</i> (Å)	8.8970(5)	9.011(7)	17.981(4)
<i>c</i> (Å)	13.0950(8)	9.022(8)	11.492(2)
α (°)	90	65.54(2)	90
β (°)	98.542(1)	84.13(3)	98.31(3)
γ (°)	90	72.48(2)	90
<i>V</i> (Å ³)	1863.5(2)	455.4(7)	1356.8(5)
<i>Z</i>	8	1	4
ρ_{calc} (g cm ⁻³)	2.142	1.878	1.739
μ (Mo K α) (mm ⁻¹)	2.511	2.929	1.813
Crystal size (mm)	0.70 × 0.30 × 0.20	0.25 × 0.17 × 0.08	0.66 × 0.32 × 0.08
Temperature (K)	153(2)	153(2)	153(2)
θ_{min} , θ_{max} (°)	2.79, 30.0	2.48, 27.7	2.17, 32.6
Dataset	–22:22, –12:12, –15:18	–8:8, –11:11, –11:11	–10:10, –27:27, –17:17
Total unique data	7950, 2706	5742, 2129	33500, 5269
Observed data [<i>I</i> > 2 σ (<i>I</i>)]	2508	2011	2767
<i>N</i> _{ref} , <i>N</i> _{par}	2706, 110	2129, 116	5269, 192
<i>R</i> , <i>wR</i> ₂ , <i>S</i> [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.0206, 0.0500, 1.077	0.0226, 0.0617, 1.117	0.0274, 0.0487, 0.625
Minimum and maximum residual density (e Å ⁻³)	0.57, –0.45	0.33, –0.39	0.40, –0.39

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

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