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Cobalt(II) compounds with acetone isonicotinoyl hydrazone tautomers: Syntheses and crystal structures of complexes with free donor atoms

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ABSTRACT

Complexes with free donor atoms, as potential metalloligands, are important building blocks in crystal engineering of coordination polymers and metal organic frameworks. In this work, the possibility of formation of cobalt(II) complexes with free N-donor atoms based on acetone isonicotinoyl hydrazone (Hisn), is verified. Syntheses, X-ray crystal structures and spectroscopic properties of two new cobalt(II) compounds with this hydrazone, are reported. The structural studies reveal the formation of a cationic complex in $[Co(Hisn)_2(H_2O)_2](NO_3)_2$ (1) containing keto ligands (Hisn) as well as a neutral complex [Co (isn)_2(py)_2]_n (2), with the deprotonated hydrazone (isn) in its enolate form. Both complexes, with two various tautomers of the hydrazone, contain uncoordinated pyridyl groups that allows to regard them as potential N-donor metalloligands.

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1. Introduction

In recent years, constructing metal-organic frameworks (MOFs), *i.e.* crystalline coordination polymers with organic ligands and potential voids, have become an increasingly popular area of materials chemistry [1–3]. The interest in these materials results mainly from their designable assembly, tunable structures as well as a variety of structure-dependent properties and applications such as for instance gas storage, separations, catalysis, optoelectronic devices, drug delivery, etc. [1-3]. MOFs are generally composed of metal ions or clusters named nodes, and organic ligands named linkers. The conceptual replacement of the latter for metalloligands (*i.e.* non-polymeric complexes containing free donor atoms) in these materials has been realized in practice with several two-step syntheses leading to mixed-metal organic frameworks [4]. This approach has also been useful for obtaining extended heterometallic networks with coordinatively unsaturated metal centers that significantly affect MOF properties such as for instance sorption selectivity, sorption capacity and catalytic performance.

A considerable number of metalloligands based on various metal centers and organic ligands have been obtained and further successfully utilized as linkers in heterometallic MOFs so far [2b,5]. In this group; however, MOFs with incorporated cobalt(II) based metalloligands are few and far between [6–11]. This may come

For cobalt, the literature survey shows an earlier report on cobalt(II) complexes with acetone isonicotinoyl hydrazone, obtained from cobalt(II) chloride [18]. However, their formulae

from the propensity of divalent cobalt to be kinetically and oxidation unstable as compared to cobalt(III) centers. For instance, such

an instability was observed in a series of cyanoacetylacetonate

metalloligands when the attempts to incorporate the cobalt(II)

metalloligand into a mixed-metal network, were unsuccessful [12].

terize cobalt(II) complexes with free N-donor atoms based on ace-

tone isonicotinoyl hydrazone (Hisn). Utilization of N-containing

heterocyclic molecules (present in Hisn and aimed to remain unco-

ordinated in its complexes) as bridging ligands in the successful

construction of coordination polymers with transition metal ions,

has been reviewed [13]. Our recent research on reactivity of the

aforementioned hydrazone (Hisn) with manganese(II) and copper

(II) centers led us either to a layered isonicotinate-based manganese-organic framework [14] or to a copper complex with free

pyridyl groups [15], respectively. Additionally, we have demon-

strated the ability of acetone picolinoyl complexes to act as

N-donor metalloligands on the example of layered homometallic

copper-organic framework built of acetone nicotinoyl μ - κ^2 , κ^1

linkers [15]. Other picolinoyl-bridged homometallic [16] and

heterometallic [17] coordination polymers with networks of higher

dimensionalities (2D or 3D) have also been reported. All these

findings underscore the feasibility of the approach to use picolinoyl

moieties (with or without metals) as building blocks for the

construction of metal-organic framework materials.

The aim of this work was to synthesize and structurally charac-







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and characterization are mainly based on elemental analysis and spectroscopic measurements, without X-ray structures. Herein we present syntheses, X-ray structures and spectroscopic properties of two new cobalt(II) monomeric complexes with acetone isonicotinoyl hydrazone. The complexes have been obtained from either acetate or nitrate cobalt salts and their single-crystal X-ray structures unequivocally confirm the diversity of hydrazone ligands in these compounds. Both complexes possess uncoordinated pyridyl groups that make them potential metalloligands with rare cobalt(II) centers.

2. Experimental

2.1. Materials and methods

All reagents and solvents were of analytical grade (Sigma Aldrich, Alfa Aesar, Polmos, Fluka) and were used without further purification. Carbon, nitrogen, and hydrogen were determined by conventional microanalysis using an Elementar Vario MICRO Cube elemental analyzer. IR spectra were recorded on a Thermo Scientific Nicolet iS5 FT-IR spectrophotometer equipped with an iD5 diamond ATR attachment. Magnetic susceptibility measurements were carried out at 22 °C on a Sherwood Scientific Magway MSB MK1 balance. Powder X-ray diffraction (PXRD) patterns were recorded at room temperature (295 K) on a Rigaku Miniflex 600 diffractometer with Cu K α radiation (λ = 1.5418 Å) in a 2 θ range from 3° to 70° with a 0.05° step at a scan speed of 3° min⁻¹.

2.2. Syntheses

2.2.1. Synthesis of $[Co(Hisn)_2(H_2O)_2](NO_3)_2$ (1)

Isoniazid (274 mg, 2.00 mmol) and acetone (700 µl, 9.52 mmol) were dissolved in ethanol (40 mL) and heated under reflux for approximately 15 min. Co(NO₃)₂·6H₂O (291 mg, 1.00 mmol) was added into colorless solution and the heating under reflux was continued for 15 min. The red mixture was left under ambient conditions and yellow precipitate of **1** was obtained after 24 h (yield: 478 mg, 83.5%). The precipitate was washed with a small amount of ethanol and dried in air. Orange crystals of 1 suitable for single-crystal X-ray diffraction were obtained after crystallization in an H-tube at room temperature. One arm of the H-tube was filled with an isoniazid/acetone solution in ethanol (ca. 3 mL; concentration the same as in the main synthesis); second arm was filled with Co(NO₃)₂·6H₂O dissolved in ethanol (*ca.* 3 mL; concentration the same as in the main synthesis); approx. 6 mL of ethanol was slowly added on top of both arms. Single crystals of 1 suitable for X-ray analysis were obtained after approx. one week. Anal. Calc. for CoC18H26N8O10: C, 37.70; H, 4.57; N, 19.54. Found: C, 37.80; H, 4.80; N, 19.46%. μ_{eff} = 4.4 μB.

2.2.2. Synthesis of $[Co(isn)_2(py)_2]$ (2)

The synthetic procedure was analogous to that of **1** except that $Co(CH_3COO)_2$ · $4H_2O$ (249 mg, 1.00 mmol) was used instead of Co $(NO_3)_2$ · $6H_2O$. The beige precipitate of **2a** (with a composition of $[Co(isn)_2(H_2O)]$) was filtered and dried in air (yield: 375 mg, 87.3%). *Anal.* for **2a**: Calc. for $CoC_{18}H_{22}N_6O_3$: C, 50.35; H, 5.16; N, 19.57. Found: C, 50.85; H, 4.83; N, 19.51%. μ_{eff} = 4.5 µB. Orange crystals of **2** suitable for single-crystal X-ray diffraction were crystallized from pyridine solution of **2a**. *Anal.* for **2**: Calc. for $CoC_{28}H_{32}N_8O_2$: C, 58.84; H, 5.64; N, 19.61. Found: C, 58.82; H, 5.40; N, 19.62%. μ_{eff} = 4.5 µB.

2.3. Crystallographic data collection and structure refinement

Diffraction data for single crystal of **1** were collected at 100 K using the Bruker-Nonius Kappa CCD four-circle diffractometer,

equipped with a Mo K α radiation source, graphite monochromator and Oxford CryoJet system for measurements at low temperature. Diffraction data for single crystal **2** were collected at 293 K on the Oxford Diffraction SuperNova four-circle diffractometer, using a Cu K α radiation source and graphite monochromator. For both compounds positions of all non-hydrogen atoms were determined by direct methods using siR-97 [19]. All non-hydrogen atoms were refined anisotropically using weighted full-matrix least-squares on F^2 . Refinement and further calculations were carried out using sHELXL-97 [20]. The hydrogen atom of the keto form of the ligand in compound **1** (H(9) bound to N(9)) was located from the difference Fourier map. The other hydrogen atoms joined to carbon atoms were positioned with an idealized geometry and refined using a riding model. The crystal data and details of data collection and structure refinement parameters are summarized in Table 1.

3. Results and discussion

3.1. Synthesis

The preparation of both compounds 1 and 2 involved condensation reaction between acetone and isonicotinoyl hydrazide as the first step that was carried out in ethanol without isolation of the resulting acetone isonicotinovl hydrazone (Hisn). Subsequently, cobalt(II) salts (nitrate or acetate) were directly added to the hydrazone solution in a 1:2 molar ratio (Scheme 1). The use of a more basic acetate salt caused deprotonation of the hydrazone and lead, after recrystallization from pyridine, to the neutral monomeric complex 2 with deprotonated enol tautomer of Hisn, i.e. acetone isonicotinoyl hydrazonate (isn). Before the final crystallization step, an intermediate precipitate of 2a was isolated. Elemental analysis, IR spectroscopy and powder X-ray diffraction have clearly shown that **2a**, with a composition corresponding to $[Co(isn)_2(H_2O)]$ formula, is different from complex 2 (Fig. 1). The insolubility of 2a in most common organic solvents may indicate its polymeric nature with coordinated pyridyl groups, similarly as it was observed for copper(II) MOF based on acetone nicotinoyl hydrazone [15]. The behavior of pyridine, capable of dissolving 2a, is unique since it acts as a base that, being in large excess, substitutes monodentately bound ligands of 2a, and at the same time does not attack bidentate enolate ligands (isn), keeping them

Table 1
Crystal data and structure refinement parameters for [Co(Hisn) ₂ (H ₂ O) ₂](NO ₃) ₂ (1) and
$[Co(isn)_2(py)_2]$ (2).

	1	2
Empirical formula	C18H26CoN8O10	C28H30C0N8O2
Formula weight	573.40	569.53
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	ΡĪ
a (Å)	7.0130(2)	8.584(5)
b (Å)	19.8350(3)	9.324(5)
c (Å)	8.9090(2)	9.470(5)
α (°)	90	97.737(5)
β(°)	98.8780(10)	102.935(5)
γ (°)	90	94.858(5)
V (Å ³)	1224.42(5)	726.8(7)
Ζ	2	1
T (K)	100(2)	293(2)
D_{calc} (Mg/m ³)	1.555	1.301
μ (mm ⁻¹)	0.770	4.943
Reflections measured	5424	12110
Reflections unique	2791 [$R_{int} = 0.0118$]	3036 [R _{int} = 0.0283]
Reflections observed $[I > 2\sigma(I)]$	2619	2892
R indices $[I > 2\sigma(I)]$		
R_1	0.0299	0.0350
wR_2	0.0762	0.0924



Scheme 1. Synthetic route to cobalt(II) complexes with acetone isonicotinoyl hydrazone: (a) cationic complex with the keto tautomer (1); (b) neutral complex with the deprotonated enol tautomer (enolate) (2).

intact. This process leads to the formation of compound 2, [Co $(isn)_2(py)_2$], with two pyridine ligands coordinated to the cobalt center.

In contrast to basic acetate, when cobalt(II) nitrate was utilized as a starting salt, the hydrazone remained in its keto form during the synthesis, and nitrates were incorporated in the resulting product **1** to balance the positive charge of cobalt ions. The as-synthesized bulk product **1** is identical with single crystals grown in the H-tube for X-ray analysis (Fig. 2). Similarly, bulk material of **2**, after reaction of **2a** with pyridine, is the same as the single-crystal used for X-ray structure determination (Fig. 2).

3.2. X-ray crystal structures

Single-crystal X-ray diffraction reveals that both monomeric complexes **1** and **2** possess a six-coordinate cobalt(II) center surrounded by two bidentate isonicotinoyl hydrazones in the *trans* mode (Figs. 3 and 4) as well as two additional monodentate ligands. The water and pyridine molecules are axially connected to cobalt(II) centers saturating coordination spheres in compounds **1** and **2**, respectively. The cobalt(II) centers in both complexes adopt octahedral geometry with deviations from ideal geometry mainly imposed by the O(8)–Co(1)–N(10) bite angles (**1**: 75.60 (4)°; **2**: 77.09(6)°) and additionally by various bonds distances (Table 2); axial shortening is observed for **1** and axial elongation for **2**. The trans geometry observed for pyridine ligands in complex **2** is different from that of analogous hydrazone complex: cis-[Co (LL)₂(py)₂] (where LL is acetone naphthoyl hydrazonoate) also obtained through recrystallization from pyridine [21].

In compound **2** the organic ligands have undergone tautomerization and deprotonation in order to compensate the charge of metal center. The different situation is in $[Co(Hisn)_2(H_2O)_2]$ $(NO_3)_2$ (**1**) where positive metal charge is compensated by two nitrate counterions. The deprotonation of the organic ligand in **2** has influence on bond lengths within the hydrazone group and the coordination sphere of this complex. The enolate form of the ligand in compound **2** can be confirmed by both crystallographic and spectroscopic data (Section 3.3). The corresponding C–N, N–N and C–O bond distances in the C=N–N(H)–C=O moiety in compound **1** show significant differences (Table 2) as compared to the corresponding bonds in compound 2, which indicates that the C=N-N(H)-C=O moiety exists in 1, whereas the conjugated $C=N-N=C-O^{-}$ moiety is present in **2**. The negative charge arising from the O8-H enolic group deprotonation, delocalized over the $C=N-N=C-O^{-}$ moiety, causes the decrease of Co(1)-O(8) bond length (2.031(2)) Å in **2**) as compared to analogous Co(1)–O(8) bond in **1** (2.115(2) Å). Furthermore, the distance between C(7)–O(8) in compound 1 is shorter than in 2 whereas the length of Co(1)-N (10) bond shows an inverse relationship (Table 2). Also, the hydrazone deprotonation in 2, that leads to a formation of the conjugated system and electron delocalization, makes the enolate ligand more planar than its keto analog in complex **1**. For example, the torsion angles O(8)-C(7)-N(9)-N(10); C(7)-N(9)-N(10)-Co(1); N(9)–C(7)–O(8)–Co(1) are 3.0(2); -18.9(2); 15.5(2)° for 1 and -1.7 (3); -3.1(2); 5.9(2)° for 2, respectively.

As also revealed by X-ray diffraction, the intermolecular interactions within crystal structure of compound **1** are dominated by relatively strong hydrogen bonds involving three groups of atoms (Table 3): nitrates oxygen atoms and hydrogen atoms of water molecules $(O(14)-H(14B)\cdots O(17)\#5 = 2.685(2) \text{ Å};$ angle = 165 $(3)^\circ$); nitrates oxygen atoms and hydrogen atoms of the hydrazone group $(N(9)-H(9)\cdots O(17) = 2.762(2) \text{ Å};$ angle = $160(2)^\circ$); pyridine nitrogen atoms and hydrogen atoms of water molecules $(O(14)-H(14A)\cdots N(1)\#4 = 2.748(2) \text{ Å};$ angle = $180(3)^\circ$). On the other hand, compound **2** is stabilized by relatively weak hydrogen bonds between hydrogen atoms of aromatic rings and nitrogen atoms of pyridyl rings or oxygen atoms of hydrazonate groups (Table 3). There is no π - π stacking between aromatic rings as the distances between their centroids are within the 4.54–5.88 Å range.

3.3. IR, UV–Vis spectroscopy and magnetic moments

The infrared spectra of the obtained complexes exhibit several characteristic absorptions of acetone isonicotinoyl hydrazone (Fig. 5). The appearance of bands at 1608 m (for 1), 1606 s (for 2) and 1596 s cm⁻¹ (for 2a) can be ascribed to v(C=N) vibrations and confirms the presence of azomethine groups. The band at 1267 cm⁻¹, observed for 2 and 2a only, indicates the presence of



Fig. 1. PXRD patterns (top) and IR spectra (bottom) of the recrystallized **2** and assynthesized **2a**. PXRD pattern given for **2** is calculated from the single-crystal structure.

enolate C–O groups and is in agreement with the crystallographic data for **2**. In contrast, the appearance of a strong band at 1622 cm⁻¹ in the spectrum of compound **1**, corresponding to the C=O stretching vibration, confirms the presence of the keto form of the hydrazone (Hisn). The methyl groups are easily recognizable by their absorptions in the 2840–3000 cm⁻¹ region, and the aromatic C–H stretching vibrations of pyridine rings appear as relatively weak bands within 3050–3100 cm⁻¹.

Both insolubility of 2a in several organic solvents and the presence of a strong band at 695 cm^{-1} in the IR spectrum of **2a** (Fig. 5), attributable to the in-plane pyridine ring deformation vibrations [22] and positively shifted from the band of the free Hisn ligand (660 cm⁻¹) [15], indicate the polymeric nature of this compound with coordinated pyridyl groups, as opposed to complex 2 with free N-donor atoms. The lack of a characteristic amide N-H stretching vibrations (\sim 3300–3500 cm⁻¹) confirms the enolization and deprotonation of the Schiff base in compounds 2 and 2a. In contrast, the spectrum of **1** contains bands of relatively high intensity at 3154 and 3181 cm⁻¹ indicating the presence of NH groups in the keto tautomer of the hydrazone. Their lowered positions are associated with the involvement of NH groups in hydrogen bonds. Additionally, the spectrum of compound 1 has a strong band at 1298 cm⁻¹ associated with symmetric stretching vibrations of the NO_3^- ions, accompanied by an intense band centered at ca.



Fig. 2. PXRD patterns of the as-synthesized bulk materials (as) compared with PXRD patterns calculated from the single-crystal structures (calc) for $[Co(Hisn)_2(-H_2O)_2](NO_3)_2$ (1) (top) and $[Co(isn)_2(py)_2]$ (2) (bottom).

1430 cm⁻¹ that was ascribed to asymmetric stretching vibrations of inorganic nitrates [22].

The room-temperature magnetic susceptibility measurements of **1**, **2** and **2a** gave the effective magnetic moments $[\mu_{eff} = (8\chi_M T)^{\frac{1}{2}}]$ **4.4**, **4.5** and **4.5** μ_B , respectively. These are reasonable values for a high-spin configuration (*S* = 3/2) for cobalt(II) centers in a tetragonal distorted environment with strong orbital contributions [23]. The spin state of these cobalt(II) compounds is in conformity with the moderate ligand field strengths for N_xO_{6-x} donor sets (*x* = 2–4). The UV–Vis spectra of **1**, **2** and **2a** support the magnetic observation.

The electronic spectra of all compounds in the solid state are dominated by strong bands in the UV region ascribable to intraligand charge-transfer transitions (at 267, 212 nm for Hisn in 1; at 242, 220 nm for py and isn⁻ in 2; at 220 nm for isn⁻ in 2a) as well as to mlct transitions observed only for enolate complexes approx. at 318, 304 nm for 2 and at 311, 304 nm for 2a (Fig. 6). The visible region contains much weaker and less pronounced absorptions associated with *d*-*d* transitions. The observed lowest energy bands and shoulders (approx. at 520sh, 487 for 1, at 550, 520sh for 2, at 560sh, 520sh for 2a, positions in nm; sh = shoulders, found as minima on the corresponding first derivative curves) can be assigned to spin-allowed ${}^{4}T_{1}(F) \rightarrow {}^{4}T_{1}(P)$ and ${}^{4}T_{1} \rightarrow {}^{4}A_{2}$ transitions for high-spin cobalt(II)-*d*⁷ complexes in an octahedral field. The increased number of other less pronounced shoulders



Fig. 3. X-ray crystal structure of $[Co(Hisn)_2(H_2O)_2](NO_3)_2$ (1): (a) cationic complex with selected atom labeling scheme and 30% displacement ellipsoids; (b) packing pattern viewed along the *a* axis; (c) packing pattern viewed along the *c* axis with strong hydrogen bonds indicated as dotted lines between donors and acceptors (d(D···A) < 2.8 Å). Hydrogen atoms are omitted for clarity.



Fig. 4. X-ray crystal structure of $[Co(isn)_2(py)_2]$ (2): (a) coordination sphere with atoms labeling scheme and 30% displacement ellipsoids; (b) packing pattern viewed along the *c* axis.

Table 2

Selected bond lengths (Å) and angles (°) for $[Co(Hisn)_2(H_2O)_2](NO_3)_2$ (1) and $[Co(isn)_2(py)_2]$ (2) with estimated standard deviations in parentheses.

	1 X = O	2 X = N
Bond lengths		
Co(1)-X(14)	2.043(2)	2.208(2)
Co(1)-O(8)	2.115(2)	2.031(2)
Co(1)-N(10)	2.157(2)	2.174(2)
C(7)-O(8)	1.247(2)	1.280(2)
C(7)–N(9)	1.335(2)	1.304(2)
N(9)-N(10)	1.407(2)	1.410(2)
N(9)-H(9)	0.86(2)	-
N(10)-C(11)	1.291(2)	1.286(2)
Bond angles		
O(8)-Co(1)-N(10)	75.60(4)	77.09(6)
O(8)-Co(1)-X(14)	89.82(5)	90.54(6)
X(14)-Co(1)-N(10)	90.47(5)	90.78(6)

Symmetry transformations used to generate equivalent atoms: #1 - x, -y, -z (for **1**); #2 - x + 1, -y + 1, -z + 1 (for **2**).

Table 3

Hydrogen bonds for $[Co(Hisn)_2(H_2O)_2](NO_3)_2$ (1) $[Co(isn)_2(py)_2]$ (2) with estimated standard deviations in parentheses (lengths in Å and angles in °).

D−H···A	d(D-H)	$d(H{\cdot}{\cdot}{\cdot}A)$	$d(D{\cdots}A)$	<(DHA)
1				
$C(5)-H(5) \cdot \cdot \cdot O(16)$	0.95	2.51	3.355(2)	148.3
C(6)−H(6)···O(16)#2	0.95	2.53	3.391(2)	151.3
C(12)−H(12B)···O(18)#3	0.98	2.56	3.506(2)	161.0
C(13)−H(13A)···O(8)#1	0.98	2.36	3.314(2)	164.2
N(9)−H(9)···O(17)	0.86(2)	1.94(2)	2.762(2)	160(2)
O(14)−H(14A)···N(1)#4	0.83(3)	1.92(3)	2.748(2)	180(3)
O(14)−H(14B)···O(17)#5	0.78(3)	1.93(3)	2.685(2)	165(3)
2				
$C(6)-H(6)\cdots N(1)#2$	0.93	2.68	3.503(3)	147.4
C(12)−H(12A)···O(8)#1	0.96	2.24	3.173(3)	164.4
C(15)−H(15)···O(8)	0.93	2.53	3.089(3)	118.7
C(18)−H(18)···N(1)#3	0.93	2.70	3.521(4)	148.3
C(19)−H(19)···O(8)#1	0.93	2.53	3.075(3)	118.1

Symmetry transformations used to generate equivalent atoms:

#1 - x, -y, -z; #2 x, -y + 1/2, z - 1/2; #3 x + 1, -y + 1/2, z + 1/2; #4 - x - 1, -y, -z - 1: #5 - x - 1, -y, -z (for 1).

#1 - x + 1, -y + 1, -z + 1; #2 - x, -y + 2, -z + 2; #3 x, y - 1, z - 1 (for **2**).



Fig. 5. ATR-IR spectra of **1**, **2** and **2a** in the $500-3500 \text{ cm}^{-1}$ range.

observed in the visible region of the spectra is the result of additional splitting of terms accompanying the symmetry reduction upon Jahn–Teller distortion. It is in agreement with X-ray crystal



Fig. 6. UV-Vis diffuse reflectance (after Kubelka-Munk transformation) of 1, 2 and 2a.

structures of **1** and **2** that show their tetragonal distortions from O_h symmetry: axial shortening and elongation, respectively (Table 2).

4. Conclusion

In conclusion, two new cobalt(II) complexes with acetone isonicotinoyl hydrazone have been obtained. Combinations of initial cobalt salts with ligand precursors led to cationic and neutral complexes containing various tautomeric forms (keto or enolate) of the hydrazone. The structural diversity of these new compounds has been confirmed by single-crystal X-ray diffraction and infrared spectroscopy. Both complexes feature free nitrogen donor atoms that may potentially be further utilized as building blocks in the construction of mixed-metal organic frameworks.

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Appendix A. Supplementary material

CCDC 980980 and 940620 contain the supplementary crystallographic data for compounds **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2016.03.045.

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