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# Supramolecular Structures of Fe(II) and Co(II) Complexes Based on the Conjugated Schiff-Base Ligands[1]

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**Absrtact**—Three new complexes $[Fe(L^1)_2(NCS)_2(CH_3OH)_2]$ (**I**), $[Co(L^2)_2(CH_3OH)_2(H_2O)_2](ClO_4)_2 \cdot L^2 \cdot 2H_2O$ (**II**), and $[Co(L^1)_3(H_2O)_2](ClO_4)_2 \cdot L^1$ (**III**) ($L^1$ = 1,4-*bis*(3-pyridyl)-2,3-diaza-1,3-butadiene; $L^2$ = 1,4-*bis*(4-pyridyl)-2,3-diaza-1,3-butadiene) have been prepared and structurally characterized by X-ray single crystall diffraction. Complexes **I** and **II** are mononuclear. Complex **III** has a 1D chain structure. Complex **I** is assembled by intermolecular O–H···N hydrogen bonds leading to 2D structure. In complex **II**, mononuclear complex cations are linked into 1D chain through hydrogen bonds. Then the chains get into 2D structure by intermolecular O–H···N hydrogen bonds too. In complex **III**, coordinated ligand $L^1$ acts as a ditopic bridge to produce 1D coordination chain. The self-complementary intermolecular O–H···N hydrogen bonds assemble the chains into 2D sheets.

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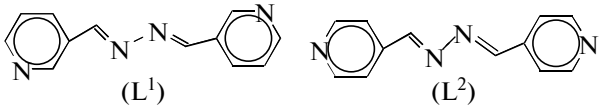
## INTRODUCTION

Schiff base ligands are very important in the development of coordination chemistry as they can readily form stable complexes with most metal ions [1–3]. The construction of new polymeric networks through the long conjugated Schiff-base ligands and metal ions is an area of intense current interest [4–7]. The structure of the ligands in building coordination networks is important. Other interactions, such as hydrogen bonding and π–π stacking, may serve as additional forces sustaining the coordination networks. Through these forces, low-dimensional coordination motifs can get into higher-dimensional architectures [8–16]. In addition, solvent molecules may also dramatically influence the architecture of the complex. Rigid organic ligands containing pyridine rings separated by various spacers, such as 4,4'-bipyridine, 1,2-*bis*(4-pyridyl)ethene, and 1,2-*bis*(4-pyridyl)ethyne, have proven popular in recent years and have resulted in a rich variety of structural motifs [17, 18]. We here report three hydrogen-bonded networks built of transition metal ion Fe(II), Co(II) and two long conjugated Schiff-base ligands 1,4-*bis*(3-pyridyl)-2,3-diaza-1,3-butadiene (**$L^1$**) and 1,4-*bis*(4-pyridyl)-2,3-diaza-1,3-butadiene (**$L^2$**):



($L^1$) ($L^2$)

[1] The article is published in the original.

## EXPERIMENTAL

All reagents were of AR grade without further purification. The $L^1$ and $L^2$ were prepared by the literature method [9]. Elemental analyses for C, H, and N were performed on a PerkinElmer 240C analyzer. The infrared spectra of the complexes in KBr pellets were obtained on a Bruker Tensor 27 IR spectrometer in the range of 4000–400 $cm^{-1}$ region.

**Synthesis of $[Fe(L^1)_2(NCS)_2(CH_3OH)_2]$ (I).** Iron(II) perchlorate hexahydrate (0.033 g, 0.1 mmol) was added to a solution of KNCS (0.02 g, 0.2 mmol) in methanol (5 mL). The mixture was stirred at room temperature for 20 min, decanted off, and filtered. The resulting colorless 1 : 2 $Fe^{2+}/NCS^-$ solution was added dropwise to a methanol solution of $L^1$ (0.042 g, 0.2 mmol, 20 mL), followed by continuous stirring for 1 h and filtration. The resulting yellow filtrate was kept at room temperature for slow evaporation. After a few days, orange single crystals suitable for X-ray analysis appeared.

For $C_{28}H_{28}N_{10}O_2S_2Fe$

| | | | |
|---|---|---|---|
| anal. calcd., %: | C, 51.22; | N, 21.33; | H, 4.30. |
| Found, %: | C, 51.18; | N, 21.40; | H, 4.31. |

FT-IR (KBr; ν, $cm^{-1}$): 2075 ν(NCS), 1618 ν(C=N), 1418 ν(O–H).

**Synthesis of $[Co(L^2)_2(CH_3OH)_2(H_2O)_2](ClO_4)_2 \cdot L^2 \cdot H_2O$ (II).** The methanol solution (10 mL) of cobalt(II) perchlorate hexahydrate (0.034 g, 0.1 mmol) was added into a solution of $L^2$ (0.042 g, 0.2 mmol) in methanol (10 mL). The mixture was stirred for 1 h and

**Table 1.** Crystallographic data and details of structure refinements for complexes **I**–**III**

| Parameter | Value | | |
|---|---|---|---|
| | **I** | **II** | **III** |
| Formula | $C_{28}H_{28}N_{10}O_2S_2Fe$ | $C_{38}H_{46}N_{12}O_{15}Cl_2Co$ | $C_{48}H_{44}N_{16}O_{10}Cl_2Co$ |
| Formula weight | 656.57 | 1040.70 | 1134.82 |
| Crystal system | Monoclinic | Triclinic | Triclinic |
| Space group | $P2_1/c$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$, Å | 9.112(3) | 9.364(3) | 10.512(6) |
| $b$, Å | 9.565(3) | 11.142(4) | 10.909(6) |
| $c$, Å | 18.280(6) | 13.338(5) | 11.714(6) |
| α, deg | 90 | 67.141(6) | 98.280(10) |
| β, deg | 94.699(6) | 80.639(6) | 99.315(9) |
| γ, deg | 90 | 78.338(6) | 92.324(9) |
| $Z$; $\rho_{calcd}$, g cm$^{-3}$ | 2; 1.373 | 1; 1.382 | 1; 1.440 |
| $\mu(MoK_\alpha)$, mm$^{-1}$ | 0.649 | 0.524 | 0.503 |
| $F(000)$ | 680 | 539 | 585 |
| Reflections measured | 8919 | 6547 | 6805 |
| Unique reflections ($R_{int}$) | 3261 (0.0281) | 4395 (0.0311) | 4561 (0.0280) |
| Reflections with ($I > 2\sigma(I)$) | 2437 | 2882 | 3008 |
| Parameters | 197 | 352 | 386 |
| GOOF ($F^2$) | 1.026 | 1.050 | 1.005 |
| $R_1$, $wR_2$ ($I > 2\sigma(I)$) | 0.0352, 0.0875 | 0.0697, 0.2036 | 0.0575, 0.1504 |
| $R_1$, $wR_2$ (all data) | 0.0549, 0.0964 | 0.1088, 0.2348 | 0.0954, 0.1798 |
| Largest diff. peak and hole, $e$ Å$^{-3}$ | 0.242 and –0.240 | 0.752 and –0.505 | 0.569 and –0.505 |

filtered to give a clear solution. Slow evaporation of the filtrate at room temperature afforded orange crystals.

For $C_{38}H_{46}N_{12}O_{15}Cl_2Co$

| | | | |
|---|---|---|---|
| anal. calcd., %: | C, 43.86; | N, 16.15; | H, 4.46. |
| Found, %: | C, 43.75; | N, 16.30; | H, 4.41. |

FT-IR (KBr; ν, cm$^{-1}$): 1618 ν(C=N), 1415 ν(O–H).

**Synthesis of $[Co(L^1)_3(H_2O)_2](ClO_4)_2 \cdot L^1$ (III).** Complex **III** was synthesized using the same procedure for complex **II** but with $L^1$ instead of $L^2$.

For $C_{48}H_{44}N_{16}O_{10}Cl_2Co$

| | | | |
|---|---|---|---|
| anal. calcd., %: | C, 50.80; | N, 19.75; | H, 3.91. |
| Found: | C, 50.91; | N, 19.63; | H, 4.01. |

FT-IR (KBr; ν, cm$^{-1}$): 1616 ν(C=N), 1409 ν(O–H).

**X-ray structure determination.** X-ray single-crystal diffraction data for complexes **I**–**III** were collected using a Bruker Smart CCD 1000 area detector at room temperature with $MoK_\alpha$ radiation (λ = 0.71073 Å). The ω scan technique was employed. The structure was solved by direct methods and refined by full matrix least-squares on $F^2$ using SHELXS-97 and SHELXL-97 programs, respectively [19]. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter. Details of the crystal parameters, data collection, and refinement are summarized in Table 1. The selected bond lengths and angles for complexes **I**–**III** are given in Table 2.

Supplementary material for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre (nos. 705571 (**I**), 705572 (**II**), and 705573 (**III**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

## RESULTS AND DISCUSSION

A view of the complex $[Fe(L^1)_2(NCS)_2(CH_3OH)_2]$ (**I**) is shown in Fig. 1. Iron atom lies in a distorted octahedron with two nitrogen atoms of $NCS^-$ (N(1), N(1*A*)) occupying the axial positions and two nitrogen atoms of $L^1$ (N(2), N(2*A*)), two oxygen atoms of $CH_3OH$ (O(1), O(1*A*) building the basal plane. Fe(1)–O(1) is 2.1034(15), Fe(1)–N(2) is 2.2535(17), and Fe(1)–N(1) is 2.1136(18) Å. The angles of O(1)Fe(1)N(1) is 87.39(7)°.

The crystal packing is shown in Fig. 2. There are intermolecular hydrogen bonds in this complex. In the crystal structure, the oxygen atoms of two coordinated $CH_3OH$ molecules in per mononuclear unit are associated with the coordinated schiff base ligands $L^1$ from neighboring units through O(1)–H(1)···N(5) hydrogen bonds (distance is 2.675 Å; angle is 155°). And in the mononuclear unit, N(5) or N(5*A*) of the coordinated Schiff base ligands $L^1$ are linked to other neighboring two mononuclear units through these hydrogen bonds, too. Extended complex gets into 2D layer structure through these hydrogen bonds and stabilized by these intermolecular hydrogen bonds.

The structure of compound **II** consists of a mononuclear $[Co(L_2)_2(CH_3OH)_2(H_2O)_2]^{2+}$ cation, two perchlorate anions and one uncoordinated $L^2$ molecule, two lattice water molecules. The structure of the complex cation is depicted in Fig. 3. Cobalt atom lies in a distorted octahedron with two oxygen atoms of $H_2O$ (O(2), O(2*A*)) occupying the axial positions and two nitrogen atoms of $L^2$ (N(1), N(1*A*)), two oxygen atoms of $CH_3OH$ (O(1), O(1*A*)) building the basal plane. The distance of Co(1)–O(2) is 2.084(2), Co(1)–O(1) is 2.133(3), and Co(1)–N(1) is 2.147(2) Å. The angles of O(2)Co(1)O(1) is 90.40(10)°.

The hydrogen bonding pattern is shown in Figs. 4, 5. In Fig. 4, mononuclear complex cations form 1D chain through the hydrogen bonds between N(4) atoms of the coordinated schiff base ligands $L^2$ molecules and O(2) atoms of coordinated water molecules. In addition, the O(2) atoms of the coordinated water molecules are linked to the uncoordinated schiff base ligands $L^2$ molecules through O(2)–H(2)···N(5) hydrogen bonds (distance is 2.033 Å; angle is 153°) and every four metal centers are interconnected to form a rhombus-like network of 13 × 9 Å in the *xy* plane. So it gets into 2D sheet structure (Fig. 5). Except O(2)–H(2)···N(4) and O(2)–H(2)···N(5) hydrogen bonds, there are intermolecular hydrogen bonds involving the oxygen atoms of coordinated methanol molecules with the oxygen atoms of uncoordinated water molecules (O(1)–H(1)···O(7) and O(7)–H(7)···O(1)), as well as the oxygen atoms of the two uncoordinated water molecules O(8)–H(8)···O(7) in this complex. But between O(8) atoms of the uncoordinated water molecules and other atoms except for O(7) atom, it doesn't have hydrogen bonds. This prevents the complex from self-assembling into 3D structures. Perchlorate anions are

**Table 2.** Selected bond lengths (Å) and angles (deg) for compounds **I–III**

| Bond | *d*, Å | Bond | *d*, Å |
|---|---|---|---|
| | **I** | | |
| Fe(1)–O(1) | 2.1034(15) | Fe(1)–N(2) | 2.2535(17) |
| Fe(1)–N(1) | 2.1136(18) | | |
| | **II** | | |
| Co(1)–O(1) | 2.133(3) | Co(1)–N(1) | 2.147(2) |
| Co(1)–O(2) | 2.084(2) | | |
| | **III** | | |
| Co(1)–O(1) | 2.051(3) | Co(1)–N(5) | 2.238(3) |
| Co(1)–N(1) | 2.180(3) | | |
| Angle | ω, deg | Angle | ω, deg |
| | **I** | | |
| O(1)Fe(1)N(1) | 87.39(7) | O(1)Fe(1)N(2) | 89.05(6) |
| O(1)Fe(1)N(2) | 90.95(6) | N(1)Fe(1)N(2) | 90.50(7) |
| N(1)Fe(1)N(2) | 89.50(7) | | |
| | **II** | | |
| O(1)Co(1)N(1) | 88.96(10) | O(2)Co(1)O(1) | 89.62(9) |
| O(2)Co(1)N(1) | 91.05(10) | | |
| | **III** | | |
| O(1)Co(1)N(1) | 91.60(12) | N(1)Co(1)N(5) | 88.11(13) |
| O(1)Co(1)N(5) | 89.15(12) | | |

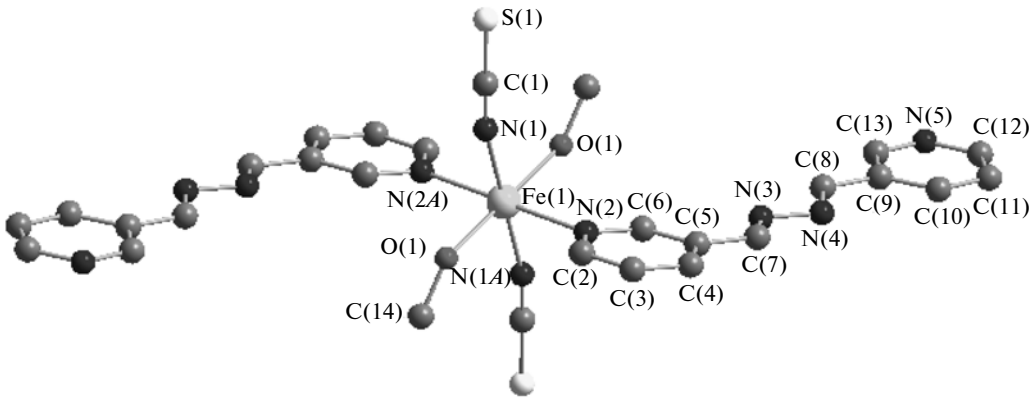



**Fig. 1.** Perspective view of the mononuclear complex in **I**.

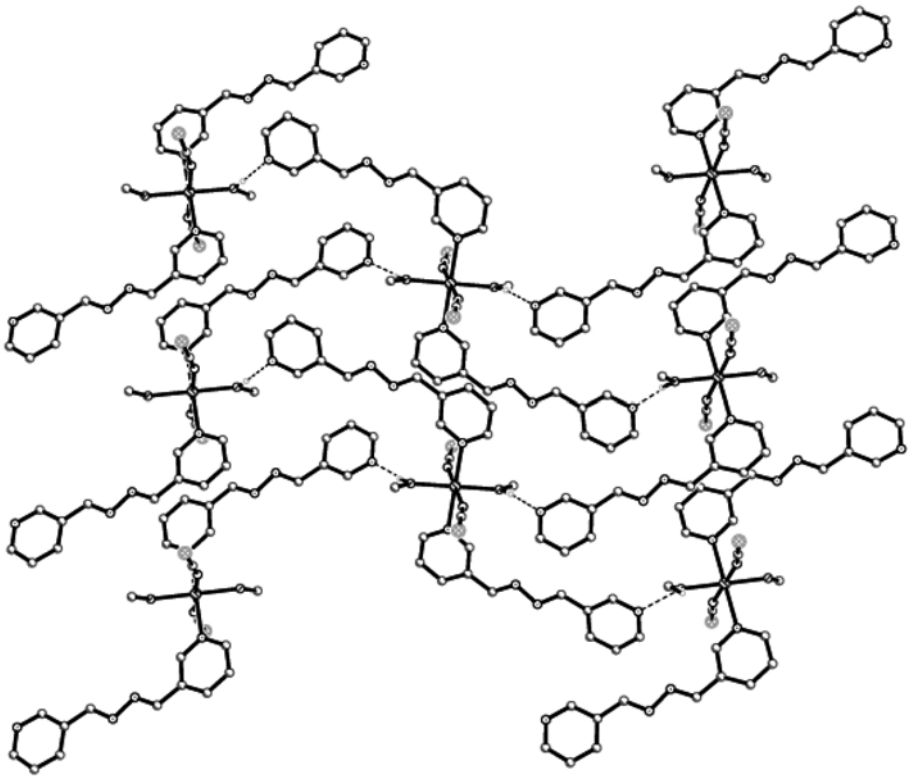


**Fig. 2.** The 2D layer in **I** assembled through the O–H···N interactions.

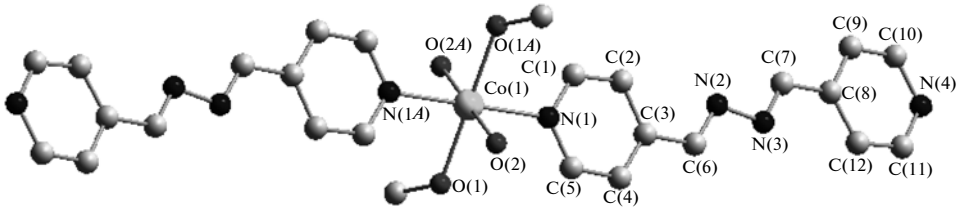



**Fig. 3.** Perspective view of the mononuclear complex cation in **II**.

located in the void space. The relevant parameters are listed in Table 3.

The structure of complex **III** consists of 1D coordination chains (Fig. 6), perchlorate ions and uncoordinated $L^1$ molecules. The 1D chains are formed through ditopic bridging $L^1$ ligands. Cobalt atom lies in a distorted octahedron with two oxygen atoms of coordinated water molecules (O(1), O(1*A*)) occupying the axial positions and four nitrogen atoms of coordinated schiff base ligands $L^1$ (N(1), N(1*A*), N(5), N(5*A*)) building the basal plane. The distance of Co(1)–O(1) is 2.051(3), Co(1)–N(1) is 2.180(3), and Co(1)–N(5) is 2.238(3) Å. The angle of O(1)Co(1)N(1) is 91.60(12)°. The nonlinear bridging mode of the

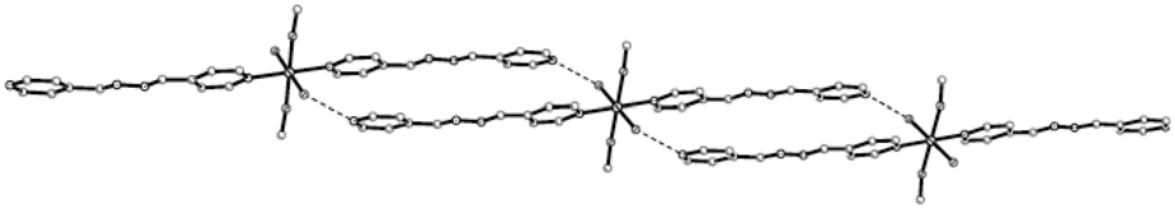


**Fig. 4.** The 1D chain structure through O(2)–H(2)···N(4) interactions in **II**.

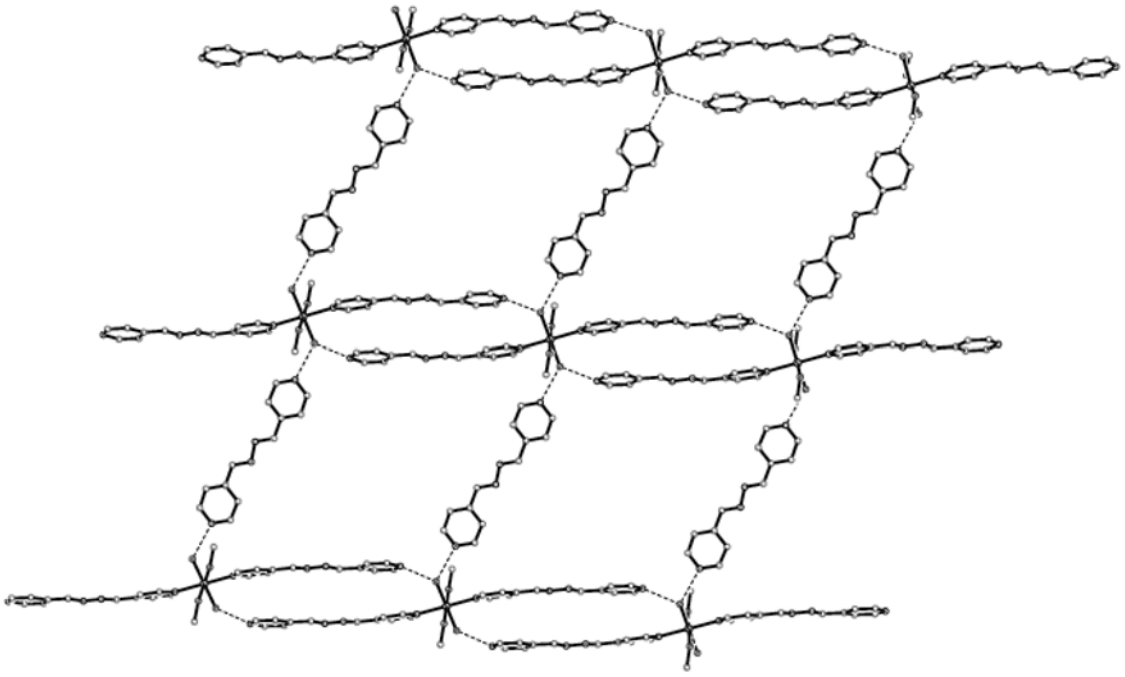


**Fig. 5.** The 2D sheet of the complex **II**. Perchlorate anions are omitted for clarity.

ligand and the local symmetry of the $Co^{2+}$ ions dictate a zigzag shape from the coordination chain, with the pyridyl groups at the corners and the Co atoms at the midpoints between the corners.

The packing of the chains structure is shown in Fig. 7. As can be seen from the figure, the O(1) atoms of coordinated water molecules are linked to the uncoordinated Schiff base ligands $L^1$ through O(1)–H(1)···N(7) hydrogen bonds (distance is 2.764 Å; angle is 167°) and leave big void space. So along the *z* direction, there are large rhombus-like networks (14 × 10 Å). The perchlorate ions are located in the void space. Through the O–H···N intermolecular hydrogen bonds, the complex gets into 2D sheet structure. This is somewhat similar to that in **II**. The relevant parameters are listed in Table 3.

In summary, we have reported three new complexes containing conjugated schiff-base ligands, and obtained mononuclear and 1D chain crystal structures. In complexes **I** and **II**, the pyridyl nitrogen atoms don't participate in direct coordination to other

**Table 3.** Geometric parameters of hydrogen bonds for complexes II and III

| Contact D–H···A | Distance, Å | | | Angle D–H···A, deg | Symmetry codes |
|---|---|---|---|---|---|
| | D–H | H···A | D···A | | |
| | | | II | | |
| O(1)–H(1)···O(7) | 0.93 | 1.85 | 2.736 | 160 | $x-1, y-1, z$ |
| O(2)–H(2a)···N(4) | 0.82 | 3.20 | 2.777 | 106 | $x-1, y-1, z+1$ |
| O(2)–H(2b)···N(5) | 0.82 | 2.03 | 2.787 | 153 | $x-1, y, z$ |
| O(7)–H(7)···O(1) | 0.86 | 2.24 | 2.736 | 117 | $x+1, y+1, z$ |
| O(8)–H(8)···O(7) | 0.88 | 2.04 | 2.700 | 131 | $-x+2, -y+1, -z+1$ |
| | | | III | | |
| O(1)–H(1a)···N(7) | 0.82 | 1.96 | 2.764 | 167 | $-x, -y, -z+2$ |
| O(1)–H(1b)···N(4) | 0.85 | 1.86 | 2.703 | 177 | $-x, -y, -z+1$ |

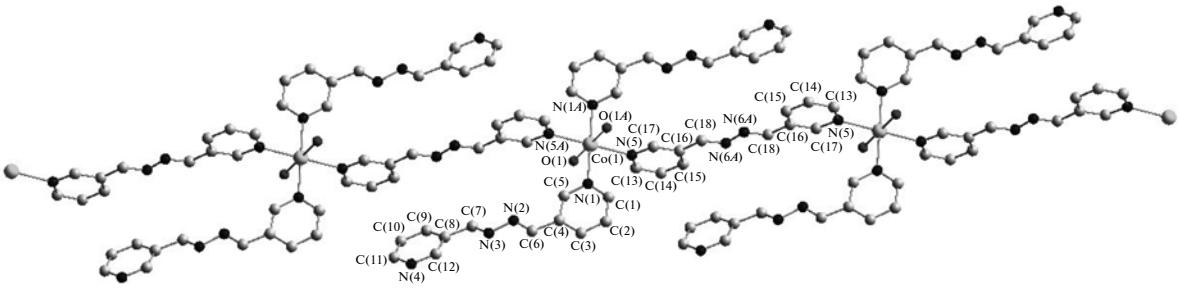



**Fig. 6.** The 1D coordination chain in **III**.

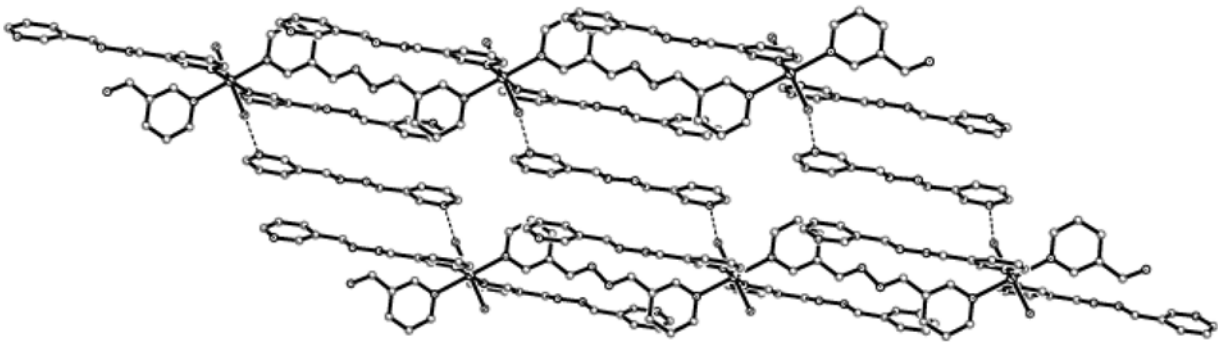


**Fig. 7.** The 2D sheet in **III** assembled through the O–H···N interactions.

metal ions, but in complex **III**, they do. They all form 2D structures through intermolecular hydrogen bonds, and large rhombus-like networks have arisen in the Co(II) complexes,

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