A Co-Crystallised Cobalt(II) Cluster of Pyridinedicarboxylic Acid (PDC) as a Luminescent Material for Selective Sensing of Methanol

Victoria T. Olayemi 1,2 · Adedibu C. Tella 1,3 · Folahan A. Adefokun 1 · Hadley S. Clayton 3 · Adetola C. Oladipo 1,4 · Gift Mehlana 5 · Adeniyi S. Ogunlaja 6 · Oluwatobi S. Oluwafemi 7 · Joseph O. Ogar 8 · Stephen P. Argent 8 · Robert Mokaya 8

Received: 29 December 2020 / Accepted: 4 May 2021

Abstract
A luminescent Cobalt(II) co-crystal \([\text{Co}_{13}(\text{PDC})_{16}(\text{H}_2\text{O})_{24.7}\text{H}_2\text{O}] \) (where \(\text{H}_2\text{PDC} = 2,6\text{-pyridinedicarboxylic acid} \)) have been prepared by oven-heating and slow evaporation of solvent. Single crystal X-ray diffraction (SCXRD) analysis revealed that \(\text{I} \) is a mixture of complexes that crystallizes in the triclinic space group \(\text{P}-1\) and the geometry around the Co(II) ions is octahedral. The structure is extensively imbued with hydrogen bonding that helps in stabilizing the complex. Thermogravimetric analysis indicates that \(\text{I} \) is thermally stable up to 364 °C. The luminescence properties of \(\text{I} \) revealed a strong emission centered at 437 nm (\(\lambda_{\text{ex}} = 345 \text{ nm} \)) assigned to ligand to metal charge transfer (LMCT). The luminescence sensing of \(\text{I} \) towards volatile organic molecules were also examined. However, \(\text{I} \) displayed a turn off towards methanol compared to other molecules with high quenching efficiency and low limit of detection (3.5 × 10^-4 vol%). The results show excellent selectively and high sensitivity.

Keywords Luminescence · Single crystal XRD · Solvothermal · Triclinic · Quenching

Introduction
Dipicolinic acid or 2,6-pyridinedicarboxylic acid has been widely used as a ligand binding to metal transition ions and may present various modes of coordination such as bidentate, tridentate, or chelate bridging via O, N, O atoms. Moreover, depending on the groups being deprotonated, dipicolinic acid can serve as either proton acceptor or proton donor [1]. Because of its low toxicity, the ligand has recently gained so much interest, making it useful in applications involving biological studies, chemical sensing and environmental remediation [2, 3]. To the best of what we know, the crystal structures of dipicolinic acid with Cu(II), Zn(II), Ni(II) and Co(III) have been reported [4–7]. Also, some other N, O-donor complexes have been studied for their photoluminescent properties [8–10].

Methanol, an aliphatic alcohol is often used as a solvent in paint manufacture, chemical and pharmaceutical industries, and as anti-freeze agent [11]. It has been known to have adverse effect on the health of human beings when it is ingested or inhaled due to its high toxicity. Acute exposure of the body to methanol vapour typically affects the central nervous system (CNS), causes headache, vertigo, fatigue, nausea,
vomiting, blurred vision, blindness and even death [12]. Yet despite its toxicity, methanol is commonly used in other areas as a cheaper and more readily available raw material. For instance, the manufacture of herbal medicines typically uses methanol as a solvent to extract natural ingredients. [13]. Thus, it is important to identify traces of methanol for the safety of consumers. Methanol is mainly determined using analytical techniques such as high performance liquid chromatography (HPLC), gas chromatography and mass spectrometry (GC-MS) [14]. While these techniques have been shown to be highly sensitive, the high cost of the equipment, immobility and the complexity of sample preparation restrict its large use in everyday life [15]. Coordination complexes have unique features such as high selectivity, quick response time, low-cost and luminescent properties resulting from weak interactions between the coordination cluster and the target analyte. Sensor technology is much simpler in instrumental implementation and sample preparation. There has been a growing interest towards synthesis of transition metal complexes as optical probes for the recognition and sensing of small organic molecules especially methanol vapour in ambient environment which will be beneficial to human health and safety. As part of our work on synthesis of transition metal complexes for sensing volatile organic molecules [16–18], a co-crystallised cluster synthesized from Cobalt(II) ion and dipicolinic acid is reported for recognition and sensing of methanol vapour.

**Experimental Section**

**Materials**

All reagents and chemicals are of analytical grade and have been used as received without further purification. 2,6-pyridinedicarboxylic acid was purchased from Sigma Aldrich, Germany, CoCl₂·2H₂O was supplied by Alfa Aesar, UK. Solvents: Ethanol (98.8%), N,N-dimethyl formamide (99.0%), methanol (99.9%), dichloromethane (99.8%), acetone (99.9%) and chloroform (99.5%) were obtained from Central Drug House (P) Ltd. New Delhi India.

**Synthesis of [Co₁₃(PDC)₁₆(H₂O)₂₄·7H₂O] 1**

In a typical reaction, 2,6-Pyridinedicarboxylic acid (0.167 g, 1 mmol) and cobalt chloride dihydrate, CoCl₂·2H₂O (0.237 g, 1 mmol) were dissolved in two separate 50 mL beakers with 10 mL ethanol and 10 mL distilled water respectively. The two solutions were gently mixed, and a clear pink solution was formed which was heated in the oven at 80 °C for 4 h. The clear solution formed was kept standing on the bench undisturbed and a crystalline purple solid was observed after 24 h. The dark purple crystals were separated from the mother liquor by filtration and then washed in ethanol-water solution (2:1 by volume) then air-dried for 30 min. Yield: 69.9%, Mp. = 364 ºC, C₁₄H₈N₂O₉Co (4094.37 gmol⁻¹). Anal. found: C; 40.70, H; 2.08, N; 6.15%. Calcd: C; 41.30, H; 1.98, N; 6.88%. IR (ATR cm⁻¹): 3441, 3195, 2317, 1707, 1543, 1372, 1245, 687, 424. UV-Vis (solid-state diffuse-reflectance) λ_max, nm (cm⁻¹); 227(44,058), 304(32,898), 435(22,991), 552(18,118), 734(13,626).

**Luminescent Sensing of Methanol**

The method described by Mehlana [19] was modified and adopted for the vapour sensing studies. 3 mg of the compounds were first activated by heating under vacuum for 5 h at 120 ºC. The activated compounds were placed in small vials and then these small vials were placed in previously evacuated larger vials containing various dry solvents (ethanol, methanol, chloroform, acetone, dimethylformamide, dichloromethane). The large vials were sealed tightly and left to stand at room temperature for 24 h (Scheme 1). The sensitivity of the compounds towards the different vapours detected were examined by exposing the compounds to different concentrations of the analytes ranging from 0.5–4.0 vol%.

**Material Characterization Techniques**

The samples were characterized by elemental analysis using an Exeter Analytical CE-440 Elemental Analyser. The infrared spectra were recorded using a Bruker Alpha diamond module FT-IR spectrometer with attenuated total reflectance (ATR) attachment for solid samples. Powder X-ray diffraction (PXRD) patterns were measured on a PANalytical X’Pert PRO diffractometer with a Cu-Kα light source (40 kV, 40 mA) with a step size of 0.02° and a 50 s time step. UV-Vis absorption spectra were measured in the solid-state in the range 200 to 800 nm using an Agilent Cary Spectrophotometer with a slit width of 2 nm. The fluorescence emission spectra were recorded on an Agilent Cary Eclipse Spectrophotometer set at 2 nm.
Fig. 1  a ORTEP view of 1 drawn at 50% ellipsoid. All hydrogen atoms are omitted for clarity. b Packing mode in 1 along b-axis, showing centroid to centroid distance. c Hydrogen bonds in 1
slit width for both the excitation and emission. TGA was performed using an SDT-Q600 TA instrument. The samples were heated in air with a heating rate of 10 °C min
−1 and the scan was recorded within the temperature range of 30–600 °C. SEM images were obtained on a Philips (FEI) XL30 SEM. The image scans reveal the morphology, shape and topology of each sample.

X-Ray Crystallography

Single crystal X-ray data for 1 was collected at 120 K on an Oxford Diffraction GV1000 diffractometer equipped with an Atlas S2 detector and a mirror-monochromated Cu-Kα radiation source. The Olex2 suite was used as a graphic user interface (GUI) and as imaging software [20]. The structures were solved with the ShelXT [21] structure solution program using Intrinsic Phasing and refined with the ShelXL [22] refinement package using Least Squares minimisation. All non-hydrogen atoms were refined with anisotropic displacement parameters and images were prepared via Mercury 4.1.0.

Refinement Experimental Details

Disorder is observed for in pyridine dicarboxylate ligand moiety H and for the entire metal-ligand complex of the residue Co3 with ligands E and F. The relative occupancies of all disorder components are refined and constrained to sum to unity. The geometries of all pyridine dicarboxylate ligand moieties are restrained to be similar (SAME). The minor disorder components are refined with isotropic displacement parameters.

Rigid bond and similarity restraints have been applied to the isotropic and anisotropic displacement parameters of all non-hydrogen atoms in the structure (RIGU, SIMU). The anisotropic displacement parameter of water residue O13W is restrained to have more isotropic character (ISOR).

The aryl hydrogen atoms were geometrically placed and refined with a riding model. Many water hydrogen atoms were observed in the electron difference map before being refined under the influence of geometric restraints on their bond distances (DFIX) and angles (DANG). The isotropic displacement parameters of all refined hydrogen atoms are fixed at 1.5 times the Ueq of their parent oxygen atom.

Where electron density peaks indicated three possible hydrogen atom positions that made plausible hydrogen bonds with nearby acceptors, hydrogen atoms were refined at all three positions with a fixed occupancy of 0.66666 each. Charge neutrality dictates that there will be an additional two protons associated with the [Co(II)3(pyridinedicarboxylate)4(H2O)4] complex residue. The location of these extra two hydrogen atoms was not clear from the electron density map; no attempt has been made to assign their whereabouts on the basis of this data. Only one hydrogen atom was observed and modelled for water ligand O11W (Fig. 1).

Results and Discussion

Description of Crystal Structure

1 crystallizes in the triclinic space group P-1, isomorphous with the corresponding Fe(II) complex reported previously [23]. a = 15.588 0 Å, b = 15.638 9 Å, c = 16.280 8 Å (Table 1). The asymmetric unit comprises of four cobalt complexes and seven lattice water. One of the complexes is trinuclear while two complexes are dinuclear and one is mononuclear. The ORTEP diagram with atom numbering is represented in Fig. 1a. The Co-O bond lengths range between 1.976(16) Å to 2.347(15) Å while the Co-N distances fall in the range 2.024(2) Å to 2.051(3) Å and are in the range usually reported in literature for cobalt complexes [24]. Also, the bond angles around the Co2+ ions in the complexes are in the range 72.1(5) to 180.00(11) which is in good agreement with literature [25]. Selected interatomic bond lengths and angles are presented in Table 2. The Co(II) ions in the

| Table 1 Crystal data collection and structure refinement for 1 |
|-----------------|-----------------|
| Details         | 1               |
| Empirical formula | C112H126Co13N16O102 |
| Formula weight  | 4094.37         |
| T (K)           | 120(2)          |
| Wavelength (Å)  | 1.54184         |
| Crystal system  | Triclinic       |
| Space group     | P-1             |
| Crystal size (mm³) | 0.629 × 0.406 × 0.296 |
| a (Å)           | 15.5880(5)      |
| b (Å)           | 15.6389(5)      |
| c (Å)           | 16.2808(6)      |
| α (°)           | 86.261(3)       |
| β (°)           | 68.559(3)       |
| γ (°)           | 76.852(3)       |
| V (Å³)          | 3596.7(2)       |
| Z               | 1               |
| \( \rho_{calc} \) (g/cm³) | 1.890             |
| F(0 0 0)        | 2077.0          |
| 2θ range for data collection (°) | 6.836 to 145.768 |
| Radiation type  | CuKα            |
| Rint            | 0.0371          |
| Data/restraints/parameters | 13,977/4282/1373 |
| Goodness-of-fit on F² | 1.028            |
| Reflections collected | 28,204           |
| \( R_1[I>2σ(I)] \) | 0.0418          |
| \( wR_2 \) (all data) | 0.1092          |
| Largest peak (e Å³) | 1.23             |
| Deepest hole (e Å³) | −1.69           |
| Bond lengths (Å) | Bond angles (°) |
|------------------|----------------|
| Co1—O8C 2.0701 (18) | O8C—Co1—O6W 84.05 (7) |
| Co1—O6W 2.1203 (18) | O8C—Co1—O7W 171.37 (7) |
| Co1—O7W 2.1154 (18) | O8C—Co1—O8W 93.42 (7) |
| Co1—O8W 2.1323 (18) | O8C—Co1—O9W 95.84 (7) |
| Co1—O9W 2.0821 (18) | O6W—Co1—O8W 176.69 (7) |
| Co1—O10W 2.0631 (18) | O7W—Co1—O8W 89.88 (7) |
| Co2—N1C 2.027 (2) | O7W—Co1—O8W 94.31 (7) |
| Co2—O9C 2.1531 (17) | O9W—Co1—O6W 90.36 (8) |
| Co2—O12C 2.1518 (19) | O9W—Co1—O7W 87.71 (7) |
| Co2—N1D 2.026 (2) | O9W—Co1—O8W 95.93 (7) |
| Co2—O9D 2.1904 (18) | O10W—Co1—O8C 86.84 (7) |
| Co2—O12D 2.1412 (17) | O10W—Co1—O9W 90.48 (8) |
| Co3—N1E 2.030 (3) | O10W—Co1—O9W 89.72 (7) |
| Co3—O9E 2.114 (3) | O10W—Co1—O9W 87.24 (8) |
| Co3—O12E 2.163 (2) | N1C—Co2—O9C 76.47 (7) |
| Co3—N1F 2.051 (3) | N1C—Co2—O12C 76.02 (8) |
| Co3—O9F 2.261 (2) | N1C—Co2—O9D 93.41 (7) |
| Co3—O12F 2.276 (2) | N1C—Co2—O12D 115.30 (7) |
| Co3X—N1Y 2.029 (12) | O9C—Co2—O9D 95.29 (7) |
| Co3X—O9Y 2.184 (10) | O12C—Co2—O9C 151.74 (7) |
| Co3X—O12Y 2.146 (12) | O12C—Co2—O9D 92.63 (7) |
| Co3X—N1X 2.035 (12) | NID—Co2—N1C 164.19 (8) |
| Co3X—O9X 2.176 (11) | NID—Co2—O9C 115.66 (7) |
| Co3X—O12X 2.127 (10) | NID—Co2—O12C 92.57 (7) |
| Co4—N1A 2.024 (2) | NID—Co2—O9D 75.97 (7) |
| Co4—O9A 2.1398 (19) | NID—Co2—O12D 76.04 (7) |
| Co4—O12A 2.1247 (18) | O12D—Co2—O9C 91.06 (7) |
| Co4—N1B 2.023 (2) | O12D—Co2—O12C 94.89 (7) |
| Co4—O9B 2.1962 (19) | O12D—Co2—O9D 151.29 (7) |
| Co4—O12B 2.1844 (18) | N1E—Co3—O9E 75.62 (10) |
| Co5—O11A 2.1604 (18) | N1E—Co3—O12E 77.23 (10) |
| Co5—O11W 2.1513 (19) | N1E—Co3—O9E 172.44 (12) |
| Co5—O2W 2.0687 (19) | N1E—Co3—O9F 103.91 (9) |
| Co5—O3W 2.046 (2) | N1E—Co3—O12F 108.30 (11) |
| Co5—O4W 2.1035 (19) | O9E—Co3—O9F 87.30 (11) |
| Co5—O5W 2.0966 (19) | O12E—Co3—O9E 152.83 (9) |
| Co6—N1G 2.024 (2) | O12E—Co3—O9F 98.06 (9) |
| Co6—O9G 2.1482 (19) | O12E—Co3—O12F 100.37 (11) |
| Co6—O12G 2.133 (2) | N1F—Co3—O9E 110.81 (11) |
| Co6—N1H 2.009 (3) | N1F—Co3—O12E 95.99 (10) |
| Co6—O9H 2.161 (2) | N1F—Co3—O9F 73.65 (9) |
| Co6—O12H 2.299 (2) | N1F—Co3—O12F 76.33 (11) |
| Co6—N1I 2.072 (2) | O12Y—Co3—O9Y 89.5 (9) |
| Co6—O9I 2.347 (15) | NIX—Co3—O9Y 98.2 (7) |
| Co6—O12I 1.976 (16) | NIX—Co3—O12Y 95.5 (8) |
| Co7—O11Hi 2.078 (2) | NIX—Co3—O9X 77.2 (6) |
| Co7—O11H 2.078 (2) | NIX—Co3—O12X 172.7 (8) |
| Co7—O11Wi 2.114 (2) | NIX—Co3—O9X 122.9 (9) |
| Co7—O11W 2.114 (2) | NIX—Co3—O12X 105.5 (8) |
| Co7—O12W 2.0517 (19) | O12Y—Co3—O9Y 92.15 (6) |
| Co7—O12Wi 2.0517 (19) | O12Y—Co3—O9X 90.8 (9) |
| Co7—O12X 2.0517 (19) | O12X—Co3—O9Y 93.7 (8) |
| Co8—O11A 2.049 (14) | O12X—Co3—O9X 152.2 (6) |
| Co8—O11B 2.049 (14) | O12X—Co3—O9Y 76.52 (8) |
| Co8—O11C 2.049 (14) | O12X—Co3—O9Z 75.78 (7) |
| Co8—O11D 2.049 (14) | O12X—Co3—O9A 91.86 (8) |
| Co8—O11E 2.049 (14) | O12X—Co3—O12B 116.04 (8) |
| Co8—O11F 2.049 (14) | O12X—Co3—O12B 92.48 (8) |
| Co8—O11G 2.049 (14) | O12X—Co3—O12B 89.19 (7) |
| Co9—O12A 2.049 (14) | O12X—Co3—O12B 150.16 (7) |
| Co9—O12B 2.049 (14) | O12X—Co3—O12B 99.24 (8) |
| Co9—O12C 2.049 (14) | O12X—Co3—O12B 93.13 (7) |
| Co9—O12D 2.049 (14) | N1B—Co4—N1A 168.13 (9) |
| Co9—O12E 2.049 (14) | N1B—Co4—O9A 107.04 (8) |
| Co9—O12F 2.049 (14) | N1B—Co4—O12A 102.33 (8) |
| Co9—O12G 2.049 (14) | N1B—Co4—O12B 76.79 (8) |
| Co9—O12H 2.049 (14) | N1B—Co4—O12B 75.62 (8) |
| Co9—O12I 2.049 (14) | O12B—Co4—O9B 151.59 (7) |
| Co9—O12J 2.049 (14) | O12B—Co4—O12B 86.94 (7) |
| Co9—O12K 2.049 (14) | O2W—Co5—O11A 91.19 (7) |
| Co9—O12L 2.049 (14) | O2W—Co5—O11A 83.10 (8) |
| Co9—O12M 2.049 (14) | O2W—Co5—O4W 97.24 (8) |
complex adopts a distorted octahedral geometry and can be grouped into two; according to the coordination environment. The first group comprising Co1 and Co7 adopts a [CoO₆] coordination environment while the second group (Co2, Co3, Co4 and Co6) with the same coordination number have a [CoO₄N₂] coordination mode. The central Co(II) ion (Co7) is surrounded by four aqua ligand and two carboxylate oxygen atoms in the same plane. Three of the complexes are fully deprotonated while two are partially deprotonated. The structures revealed some π–π interactions arising from the pyridine rings of the mononuclear and trinuclear complexes with a centroid-centroid distance of 3.655 Å (Fig. 1b). The Co⋯Co intercluster separations are in the range 5.992 Å–6.828 Å shorter than reported ones [26]. The interstitial water molecules form a hydrogen bond network that bridges between the four complex cations in the asymmetric unit. Hydrogen bonds are also observed directly between the coordinated water ligands and donor and acceptor atoms of adjacent complexes. A network of intermolecular hydrogen bonding was also observed (Fig. 1c). The selected hydrogen bonding parameters for 1 are shown in Table 3.

FTIR Spectra

The FTIR spectrum of the ligand revealed the characteristic absorption bands of ν(C=O) and ν(C-O) at 1583 cm⁻¹ and 1305 cm⁻¹. These absorption bands were shifted to 1608 cm⁻¹ and 1284 cm⁻¹ respectively in the spectrum of 1 suggesting coordination of the Co(II) ion to the ligand (Fig. S1). The sharp peaks at 1572 cm⁻¹ and 1370 cm⁻¹ are assigned to the

Table 2 (continued)

| Bond lengths (Å) | Bond angles (°) |
|------------------|-----------------|
| O2W—Co5—O5W     | 174.38 (8)      |
| O3W—Co5—O11A    | 177.38 (8)      |
| O3W—Co5—O1W     | 92.24 (8)       |
| O3W—Co5—O2W     | 91.19 (8)       |
| O3W—Co5—O4W     | 86.65 (8)       |
| O3W—Co5—O5W     | 92.96 (8)       |
| O4W—Co5—O11A    | 94.16 (7)       |
| O4W—Co5—O1W     | 178.84 (8)      |
| O5W—Co5—O11A    | 84.59 (7)       |
| O5W—Co5—O1W     | 92.95 (8)       |
| O5W—Co5—O4W     | 87.39 (8)       |
| N1G—Co6—O9G     | 76.01 (8)       |
| N1G—Co6—O12G    | 76.79 (8)       |
| N1G—Co6—O9H     | 88.43 (10)      |
| N1G—Co6—O12H    | 120.13 (9)      |
| N1G—Co6—N1I     | 168.2 (16)      |
| N1G—Co6—O9I     | 100.3 (4)       |
| O9G—Co6—O9H     | 97.58 (8)       |
| O9G—Co6—O12H    | 90.64 (7)       |
| O9G—Co6—O9I     | 93.8 (5)        |
| O12G—Co6—O9G    | 151.10 (8)      |
| O12G—Co6—O9H    | 91.01 (10)      |
| O12G—Co6—O12H   | 94.87 (8)       |
| O12G—Co6—O9I    | 100.3 (5)       |
| N1H—Co6—N1G     | 164.10 (17)     |
| N1H—Co6—O9G     | 113.0 (3)       |
| N1H—Co6—O12G    | 95.8 (3)        |
| N1H—Co6—O9H     | 77.61 (11)      |
| N1H—Co6—O12H    | 74.00 (10)      |
| O9H—Co6—O12H    | 151.44 (10)     |
| N1I—Co6—O9G     | 113 (2)         |
| N1I—Co6—O12G    | 95 (2)          |
| N1I—Co6—O9I     | 72.1 (5)        |
| O12I—Co6—N1I    | 108.6 (5)       |
| O12I—Co6—O9G    | 91.1 (5)        |
| O12I—Co6—O12G   | 88.7 (6)        |
| O12I—Co6—N1I    | 79.7 (6)        |
| O12I—Co6—O9I    | 151.0 (6)       |
| O11H—Co7—O11Hi  | 180.00 (11)     |
| O11H—Co7—O11Wi  | 91.86 (8)       |
| O11H—Co7—O11W   | 88.14 (8)       |
| O11Hi—Co7—O11W  | 91.86 (8)       |
| O11Hi—Co7—O11Wi | 88.14 (8)       |
| O11Wi—Co7—O11W  | 180.0          |
| O12W—Co7—O11H   | 87.65 (9)       |
| O12W—Co7—O11Hi  | 87.65 (9)       |
| O12W—Co7—O11H   | 92.35 (9)       |
| O12W—Co7—O11Wi  | 92.36 (9)       |
| O12W—Co7—O11W   | 88.62 (9)       |
| O12W—Co7—O11   | 91.38 (9)       |
| O12W—Co7—O12W   | 91.38 (9)       |
| O12W—Co7—O12   | 180.00 (2)      |
Table 3  Selected hydrogen bonding parameters of 1

| D—H···A     | D—H (Å) | D···A (Å) | H···A (Å) | D—H···A (°) |
|-------------|---------|-----------|-----------|-------------|
| O8F—H8F···O9B || 0.84 (2) | 2.658 (3) | 1.84 (2) | 166 (5)     |
| C4H—H4H···O9F || 0.95 | 2.820 (4) | 2.20 | 122         |
| C3X—H3X···O11Xii | 0.95 | 2.69 (2) | 1.88 | 142         |
| O1W—H1WA···O11Fiv | 0.82 (4) | 2.895 (7) | 2.08 (4) | 171 (4)     |
| O1W—H1WA···O11Yiv | 0.82 (4) | 2.83 (4) | 2.03 (6) | 165 (4)     |
| O1W—H1WB···O11D | 0.86 (4) | 2.809 (3) | 1.96 (4) | 170 (4)     |
| O2W—H2WA···O13W | 0.87 (4) | 2.692 (3) | 1.84 (4) | 167 (4)     |
| O2W—H2WB···O9H | 0.87 (2) | 2.641 (3) | 1.78 (2) | 172 (4)     |
| O2W—H2WB···O9I | 0.87 (2) | 2.741 (15) | 1.89 (3) | 168 (4)     |
| O3W—H3WA···O12D | 0.85 (4) | 2.712 (3) | 1.88 (4) | 169 (4)     |
| O3W—H3WB···O11Xiii | 0.79 (4) | 2.657 (3) | 1.87 (5) | 179 (5)     |
| O4W—H4WA···O12A | 0.89 (4) | 2.680 (3) | 1.85 (4) | 155 (4)     |
| O4W—H4WB···O8H | 0.78 (4) | 2.627 (3) | 1.85 (4) | 170 (4)     |
| O4W—H4WB···O8I | 0.78 (4) | 2.877 (15) | 2.11 (4) | 166 (4)     |
| O5W—H5WA···O18Wiiii | 0.82 (6) | 2.769 (3) | 1.97 (6) | 163 (6)     |
| O6W—H6W···O11Bv | 0.76 (4) | 2.752 (3) | 2.00 (4) | 174 (4)     |
| O6W—H6WA···O19W | 0.85 (2) | 2.769 (3) | 1.92 (2) | 171 (4)     |
| O7W—H7WA···O12Bv | 0.91 (4) | 2.714 (3) | 1.81 (4) | 171 (3)     |
| O7W—H7WB···O11Dvii | 0.79 (4) | 2.723 (3) | 1.95 (4) | 168 (4)     |
| O8W—H8WA···O9C | 0.77 (4) | 2.817 (3) | 2.08 (4) | 159 (4)     |
| O8W—H8WB···O8G | 0.88 (4) | 2.678 (3) | 1.80 (4) | 175 (4)     |
| O9W—H9WA···O8E | 0.79 (4) | 2.686 (4) | 1.90 (4) | 175 (4)     |
| O9W—H9WA···O8X | 0.79 (4) | 2.71 (2) | 1.93 (5) | 167 (4)     |
| O9W—H9WB···O9G | 0.82 (4) | 2.691 (3) | 1.87 (4) | 173 (4)     |
| O10W—H10A···O15Wvii | 0.81 (2) | 2.800 (3) | 1.99 (2) | 179 (4)     |
| O10W—H10B···O11Eviii | 0.82 (2) | 2.741 (7) | 1.93 (2) | 172 (4)     |
| O10W—H10B···O11Yviii | 0.82 (2) | 2.70 (4) | 1.89 (5) | 176 (4)     |
| O11W—H11W···O9Aii | 0.76 (5) | 2.749 (3) | 2.00 (5) | 168 (5)     |
| O17W—H17B···O11Cix | 0.85 (2) | 2.503 (3) | 1.66 (2) | 170 (7)     |
| O12W—H12A···O8E | 0.81 (4) | 2.614 (4) | 1.83 (5) | 163 (4)     |
| O15W—H13B···O12D | 0.90 (5) | 2.893 (3) | 2.01 (5) | 169 (5)     |
| O14W—H14A···O8Dix | 0.80 (4) | 2.490 (3) | 1.69 (4) | 171 (6)     |
| O14W—H14B···O12H | 0.83 (2) | 2.701 (3) | 1.94 (3) | 153 (5)     |
| O14W—H14B···O11I | 0.83 (2) | 2.294 (17) | 1.72 (6) | 124 (6)     |
| O14W—H14B···O12I | 0.83 (2) | 2.611 (16) | 1.92 (4) | 140 (5)     |
| O14W—H14W···O16W | 0.80 (2) | 2.505 (3) | 1.78 (4) | 150 (7)     |
| O15W—H15A···O9Dix | 0.81 (5) | 2.856 (3) | 2.05 (5) | 174 (4)     |
| O16W—H16A···O14W | 0.83 (2) | 2.505 (3) | 1.78 (2) | 145 (4)     |
| O16W—H16W···O9Ei | 0.82 (2) | 2.773 (3) | 2.29 (4) | 119 (4)     |
| O17W—H17A···O11Gi | 0.84 (2) | 2.529 (3) | 1.71 (2) | 165 (4)     |
| O17W—H17W···O8B | 0.84 (2) | 2.604 (3) | 1.79 (2) | 163 (4)     |
| O18W—H18W···O12F | 0.85 (1) | 2.855 (4) | 2.09 (3) | 148 (4)     |
| O18W—H18A···O5Wiiii | 0.85 (2) | 2.769 (3) | 1.92 (2) | 174 (4)     |

Symmetry codes: (i) −x + 1, −y + 1, −z; (ii) −x + 1, −y + 1, −z + 1; (iii) −x + 1, −y, −z + 1; (iv) x + 1, y, z; (v) x, y, z − 1; (vi) −x + 2, −y, −z; (vii) x, y − 1, z; (viii) −x + 1, −y, −z; (ix) x, y + 1, z
antisymmetric and symmetric vibrations respectively. The broad absorption band in the region 3101 to 3466 cm\(^{-1}\) is characteristic of \(\nu(O-H)\) of coordinated and lattice water. Additionally, a sharp absorption band due to aromatic \(\nu(C-N)\) stretching vibration was observed at 1187 cm\(^{-1}\), this band was seen at higher frequency in the spectrum of the free ligand. This indicates pyridine N-group chelation to the Co(II) center [27]. The weak peaks at 532 cm\(^{-1}\) and 428 cm\(^{-1}\) are assigned to \(\nu(Co-N)\) and \(\nu(Co-O)\) respectively.

**Electronic Spectra**

The electronic data of 1 and its ligands were recorded in the solid state at room temperature in the range 200 nm to 800 nm.
as shown in Fig. S2. The H$_2$PDC ligand showed absorption bands at 238 nm and 271 nm which are characteristic of the carboxylic acid and pyridine chromophores. The absorption bands of the ligand are assigned to $\pi \rightarrow \pi^*$ electronic transitions. Compound 1 reveals absorption bands in the visible region at 431 nm and 731 nm with a shoulder at 547 nm. These absorption bands are assigned to $4T_1g (F) \rightarrow 4T_2g$, $4T_1g (F) \rightarrow 4T_1g (P)$, and $4T_1g (F) \rightarrow 4A_2g$ of the spin allowed transitions of the octahedral Co$^{2+}$ ions, respectively [28].

Thermogravimetric Analysis

The TGA curve of 1 revealed a three-step decomposition fashion (Fig. 2a). The first step showed a loss of seven molecules of lattice water and six molecules of coordinated water in the temperature range between 111 °C to 149 °C, 10.95% found (calc. 9.70%). The second decomposition step corresponds to the loss of Co$_3$(PDC)$_4$ and 2[Co$_2$(PDC)$_2$] moieties of weight 51.94% found (calc. 53.87%). The final weight loss in the temperature range 361 °C to 402 °C corresponds to the loss of 2[Co$_2$(PDC)$_2$] and 2[Co(PDC)$_2$] moieties leaving a residue of 22.34% found (calc. 23.91%) CoO.

Furthermore, scanning electron micrographs (SEM) for the cobalt complex was recorded and shown in Fig. 2b. SEM provides high resolution and clear images of the particles of the examined compounds, which helps in understanding the morphological changes upon metal complexation. The SEM micrograph shows prism-like homogenous aggregate morphology of the complex having tiny uniform crystals at the surface.

Photoluminescent Property

The photoluminescence (PL) spectra of 1 and the parent ligand were recorded in solid-state at room temperature (Fig. 2c). The ligand displayed a distinct emission band with high
intensity centred at 437 nm ($\lambda_{ex} = 345$ nm). The emission band is assigned to n $\rightarrow$ $\pi^*$ / $\pi^*$ $\rightarrow$ $\pi^*$*. Compound 1, showed a similar emission at 437 nm ($\lambda_{ex} = 345$ nm) but with much lower intensity which may be due to the partially filled d orbital of the Co$^{2+}$ (3d$^7$) ion leading to Ligand to Metal charge transfer (LMCT) [29, 30]. The similarity in the emission wavelength of the free ligand and the title compound suggests that the luminescence of 1 is attributed to ligand-based emissions [31].

**Sensing of Volatile Organic Molecules**

The PL spectra of 1 upon exposure to different organic molecules is presented in Fig. 3a. From the structural and fluorescent properties of the Co(II) complex, it is expected that the free water molecules could be exchanged with other type of small organic molecules. The luminescence intensities are highly dependent on the solvents and their selectivity is in the sequence DMF > CHCl$_3$ > DCM > Acetone > EtOH > MeOH with a quenching efficiency of 79% (Fig. S3). To investigate the sensitivity of 1 towards methanol, it was exposed to the solvent in varying concentrations. Gradual decrease in photoluminescence emission intensities were observed upon increasing the concentration of methanol leading to about 97% quenching at 4.0 vol% acetone content (Fig. 3b). However, the phenomenon of energy transfer can be used to explain the quenching mechanism. The photoluminescent emission of 1 is highly dependent on Ligand to metal charge transfer, therefore, it is logical to suggest that interaction of methanol molecules with the ligand may disrupt energy transfer from ligand to Co$^{2+}$ thereby, drastically quenching the luminescence of the complex (Fig. 3c). This mechanism is similar to those proposed in previous literature [32]. Furthermore, thermogravimetric analysis revealed that the activated complex was stable up to 246 °C indicating the lattice is free of solvent molecules prior to interaction with methanol molecules. The TGA curve of 1@methanol reveals the loss of methanol at 68 °C. (Fig. 3d). As shown in Fig. S4, the spectrum of 1@activated revealed a partial disappearance of the broadband observed in the region 3101–3466 cm$^{-1}$ ($\nu$(OH)) in the spectrum of the as-synthesised complex. This is ascribed to the removal of lattice water upon activation. Moreover, the FTIR spectrum of 1@MeOH displayed new peaks found between 2825 and 3131 cm$^{-1}$ corresponding to $\nu$(O-H) stretching of alcohol this indicates the presence of MeOH. PXRD pattern of 1 before and after interaction with methanol remains identical depicting the structural rigidity of the complex (Fig. S5).

In addition, the Stern Volmer plot also displayed excellent linearity ($R^2 = 0.9789$) in the methanol concentration range from 0.5 to 4.0 vol% and the quenching constant ($K_{sv}$) was
9.03 × 10⁻³ /vol% while the limit of detection (LOD) was found to be 0.00035 vol% which is below the permissible occupational exposure limit for methanol (0.025 vol%) [33]. Noteworthy colour changes were also observed with the naked eye before and after solvent vapour interaction as the displayed in the photographs in Fig. S6.

**Computational Details for the Proposed Interaction Study**

Density functional theory (DFT) was employed to understand the mode of interactions between a unit of 1 and solvents (C₂H₅OH and CH₃OH). Geometry optimisations and vibrational analyses of 1-C₂H₅OH (CH₃OH) complexes were performed using the Gaussian16 software [34]. B3LYP [35] functional was employed with a 6-311 g++(d,p) basis set was employed for atoms C, H, O, N and Cl, while LANL2DZ for Na. The binding energy of formation was calculated by using Eq. 1 below.

\[
BE = E_{\text{complex}} - (E_1 + E_{\text{solvents}})
\]  

(1)

The NBO and MEP for the compounds were also calculated. Optimized molecules were obtained with Chemcraft visualization program.

**Theoretical Studies: Optimization Studies and Binding Energies**

Interaction studies between 1 and alcohols (CH₃OH and C₂H₅OH) was carried out because these molecules provide electron donating atom (O) for coordination/interaction with

| Complex                                      | HOMO   | LUMO   | Energy Gap |
|----------------------------------------------|--------|--------|------------|
| [Co₁₃(PDC)₁₆(H₂O)₂₄•7H₂O] (1)                  | −11.966| −10.976| 0.99       |
| [Co₁₃(PDC)₁₆(H₂O)₂₄•7H₂O] (1)-CH₃OH            | −9.967 | −8.778 | 1.19       |
| [Co₁₃(PDC)₁₆(H₂O)₂₄•7H₂O] (1)-C₂H₅OH           | −10.243| −2.432 | 7.81       |

---

**Fig. 5** HOMO-LUMO positions of 1 (a,b), 1-CH OH (c,d) and 1-C₂H₅OH (e,f)
1. The geometry of 1 was optimized using a unit of the crystal and it was observed that the structure were very similar to those of the X-ray diffraction unit. Furthermore, optimized structures presented close bond distance parameters compared to the crystal structure unit as shown in Fig. 4a. The optimization of 1-C2H5OH and 1-CH3OH (Fig. 4b and c) presented octahedral compounds coordinating via oxygen atom of alcohols to metal center (Co), with 1-C2H5OH presenting more favourable octahedral structure due to the observed low distortion.

The binding energies of 1 with C2H5OH and CH3OH relate to the feasibility of interaction between molecules. 1-CH3OH (−413.2 au) presented the smallest binding energies compared to 1-C2H5OH (−154.1 au) (Table 4). The more negative binding energies confirmed the feasibility of interaction between 1 and CH3OH.

**HOMO-LUMO Analysis**

The difference between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) (HOMO–LUMO gap) describes the polarizability and reactivity of molecules, and it predicts reactivity between species by providing the electrical transport properties as well as electron carrier and mobility in molecules [36, 37]. The images of HOMO and LUMO orbitals for 1, 1-C2H5OH and 1-CH3OH are shown in Fig. 5a–f. Generally, LUMO positions are distributed around ligand atoms (nitrogen (N), oxygen (O) and carbon (C)) and metal center (Co). HOMO is mostly centered around non-metals including nitrogen (N), oxygen (O) and carbon (C)). The change in HOMO and LUMO energies before and after adduct formation indicated an electron density transfer within the complexes/adducts. The HOMO, LUMO and band gap energies of the various complexes/adducts are provided in Table 5. Adduct, 1-CH3OH presented the least HOMO–LUMO energy gap which further confirms possible interactions. Adducts formed between 1 and CH3OH clearly indicated that the interaction is mainly driven by electron donation from HOMO to LUMO.

**Conclusions**

In summary, we have successfully synthesized a co-crystallised cobalt cluster with dipicolinate ligand comprising of hexacoordinated cobalt centers. The complex possesses excellent luminescence properties by virtue of extended π-conjugation of the ligand. It exhibited selective sensing of methanol over other small organic molecules in a luminescence turn-off fashion. Moreover, negligible effect from other organic solvents such as ethanol, acetone, chloroform, dichloromethane and dimethylformamide was observed. The quenching mechanism could be described as resulting from energy transfer from the electron rich complex to methanol. Furthermore, PXRD, TGA and FTIR has confirmed the selective recognition of methanol vapour. The small binding energy and low energy gap obtained by theoretical analysis confirms possible interactions between complex 1 and methanol. These results authenticate the prospect of designing cheap transition metal complexes with suitable ligands for probing volatile organic molecules.

**Supplementary Information** The online version contains supplementary material available at https://doi.org/10.1007/s10895-021-02746-9.

**Acknowledgements** The authors appreciate the Royal Society of Chemistry for funding and the School of Chemistry, University of Nottingham for X-ray crystallography analysis of the compounds. We are grateful to the Center for High Performance Computing (CHPC), Capetown, South Africa for providing the platform to carry out molecular modelling studies using the Gaussian16 software.

**Data Availability (Data Transparency)** CCDC 1999482 contains the crystallographic data which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

**Code Availability (Software Application or Custom Code)** ChemDraw, Mercury 3.1. Geometry optimisations and vibrational analyses were performed using the Gaussian16 software (Frisch et al., 2016). B3LYP functional was employed with a 6-311 g++(d,p) basis set for atoms C, H, O, N and Cl, while LANL2DZ for Na (Becke et al., 1993).

**Authors Contributions** Adedibu C. Tella: Conceptualization, Supervision, Writing – review & editing, and design of study.
Victoria T. Olayemi: Data curation, Formal analysis, Methodology, Writing -original draft.
Folahan A. Adekola: Supervision, Writing – review & editing of the revised version.
Hadley S. Clayton: Supervision, Writing - review & editing.
Adetola C. Oladipo: Data curation, Formal analysis, Methodology, Writing - original draft.
Gift Mehlana: Conceptualization, Supervision, Writing - review & editing.
Adeniyi S. Ogunlaja: Conceptualization, Supervision, Writing - review.
Oluwatobi S. Oluwafemi: Supervision, Writing - review & editing.
Joseph O. Ogar: Single crystal analyses and interpretation, Supervision, Writing - review & editing.
Stephen P. Argent: Single crystal analyses and interpretation, Supervision, Writing - review & editing, and design of study.
Robert Mokaya: Conceptualization, Supervision, Writing - review & editing, and design of study.

**Funding** This research work is funded by the Royal Society of Chemistry under the Researcher Mobility Grant.

**Declarations**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
References

1. Li D, Zhong GQ (2014) Synthesis, crystal structure, and thermal decomposition of the cobalt(II) complex with 2-picolinic acid. Sci World J 2014:1–7. https://doi.org/10.1155/2014/641608

2. Swamy GYSK, Sivanarayanan P, Sridhar B, Joshi LR (2016) Crystal structure studies and antimicrobial activities of transition metal complexes of pyridine-2,6-dicarboxylic acid and imidazole containing water clusters. J Coord Chem 69:1602–1617. https://doi.org/10.1080/00958972.2016.1175558

3. Andres J, Chauvin AS (2010) Europium complexes of tris(dipicolinato) derivatives coupled to methylumbelliferone: a double sensitization. Eur J Inorg Chem 2010:2700–2713. https://doi.org/10.1002/ejic.201000126

4. Aghabozorg H, Ghadermazi M, Zabihi F, Nakhjavan B, Soleimannejad I, Sadr-Khanlou E, Moghimi A (2008) Novel complexes of zinc(II) with different proton transfer ion pairs obtained from dipicolinic acid: synthesis, characterization and x-ray crystal structure. J Chem Crystallogr 38:645–654. https://doi.org/10.1007/s10870-008-9363-5

5. Ramirez D, Martinez JD, Araujo ML, Brito F, Perez A, Hernandez L, Del Carpio E, Lubes V (2016) Ternary complex formation between nickel(II)-Dipicolinic acid with small blood serum bioligands. J Mol Liq 221:744–747. https://doi.org/10.1016/j.molliq.2016.06.068

6. Luo JH, Hong MC, Shi Q, Liang YC, Zhao YJ, Wang RH, CaO R, Weng JB (2002) Synthesis, structure and magnetic properties of a quasi-two-dimensional compound [Cu(C5H4NCOO)2]·2H2O. Transition Metal Chemistry 27:311–315. https://doi.org/10.1023/A:1014876514184

7. Novitski G, Borta A, Shova S, Kazheva ON, Gidane M, SimonovYA (2008) Synthesis and structure of Co(III) complexes with 2-pyridinocarboxylic acid. Russ J Inorg Chem 53:202–208. https://doi.org/10.1134/S0036023608020095

8. Majumdar D, Das S, Thomas R, Ullah Z, Sreejith SS, Das D, Shukla P, Bankura K, Mishra D (2019) Syntheses, X-ray crystal structures of two new Zn(II)-dicyanamide complexes derived from H2vanen-type compartmental ligands: investigation of photoluminescence, in vitro cytotoxic effect and DFT-TDDFT studies. Inorganica Chim Acta 492:221–234. https://doi.org/10.1016/j.ica.2019.04.041

9. Majumdar D, Agrawal Y, Thomas R, Ullah Z, Santra MK, Das S, Pal TK, Bankura K, Mishra D (2020) Syntheses, characterization, crystal structures, DFT/TF-DFT, luminescence behaviors and cytotoxic effect of bicomponental Zn(II)-dicyanamide Schiff base coordination polymers: an approach to apoptosis, autophagy and necrosis type classical cell death. Appl Organomet Chem 34:1–22. https://doi.org/10.1002/aoc.5269

10. Majumdar D, Das D, Sreejith SS, Das S, Kumar Biswas J, Mondal M, Ghosh D, Bankura K, Mishra D (2019) Dicyanamide-interlaced assembly of Zn(II)-schiff-base complexes derived from salicyaldimeino type compartmental ligands: syntheses, crystal structures, FMO, ESP, TD-DFT, fluorescence lifetime, in vitro antibacterial and anti-biofilm properties. Inorganica Chim Acta 489:244–254. https://doi.org/10.1016/j.ica.2019.02.022

11. Besheli ME, Rahimi R, Farahani YD, Safarifard V (2019) A porous Ni-based metal-organic framework as a selective luminescent probe to Fe3+ metal ion and MeOH. Inorganica Chim. Acta. 495:118956. https://doi.org/10.1016/j.ica.2019.118956

12. Wang ML, Wang JT, Choong YM (2004) A rapid and accurate method for determination of methanol in alcoholic beverage by direct injection capillary gas chromatography. J Food Compos Anal 17:187–196. https://doi.org/10.1016/j.jfca.2003.08.006

13. Mousavi SR, Namazi-Ghassemi M, Layegh M, AftabAghae M, Vafaee M, Zare G, Moghimpan T, Mood MB (2011) Determination of methanol concentrations in traditional herbal waters of different brands in Iran. Iran J Basic Med Sci 14:361–368. https://doi.org/10.22038/ijbms.2011.5025

14. Xu X, Fillos J, Ramalingam K, Rosenthal A (2012) Quantitative analysis of methanol in wastewater by GC-MS with direct injection or headspace SPME sample introduction. Anal Methods 4:3688–3694. https://doi.org/10.1039/c2ay25452b

15. Jin Z, He H, Zhao H, Borjigin T, Sun F, Zhang D, Zhu G (2013) A luminescent metal-organic framework for sensing methanol in ethanol solution. Dalton Trans. 42:13335–13338. https://doi.org/10.1039/c3dt51414e

16. Tella AC, Owalude SO, Alimi LO, Oladipo AC, Olatunji SJ, Adeyemi OG (2016) Facile synthesis and vapochromic studies of Co(II) complexes bearing NO and OO donor ligands. Egypt J Basic Appl Sci 3:125–133. https://doi.org/10.1016/j.ejbas.2015.12.001

17. Tella AC, Owalude SO, Omosoto MF, Olatunji SJ (2017) Synthesis , crystal structures and luminescence properties of new multi-component co-crystals of isostructural Co (II) and Zn (II) complexes Synthesis, crystal structures and luminescence properties of new multi-component co-crystals of isostructura. J Mol Struct 1157:450–456. https://doi.org/10.1016/j.molstruc.2017.12.086

18. Tella AC, Owalude SO, Omosoto MF, Olatunji SJ, Ogunlaja AS, Alimi LO, Popoola OK, Bourne SA (2018) Synthesis, crystal structures and luminescence properties of new multi-component co-crystals of isostructural Co(II) and Zn(II) complexes. J Mol Struct 1157:450–456. https://doi.org/10.1016/j.molstruc.2017.12.086

19. Melhana G, Ramon G, Bourne SA (2013) Alcohol responsive 2D coordination network of 3-(4-pyridyl)benzoate and Zinc(II). Zeitschrift Fur Krist 228:318–322. https://doi.org/10.1524/zkri.2013.1607

20. Dolomanov OV, Boshits LJ, Gildea RJ, Howard JAK, Puschmann H (2009) OLEX2: a complete structure solution, refinement and analysis program. J Appl Crystallogr 42:339–341. https://doi.org/10.1107/S0021889808027226

21. Sheldrick GM (2015) SHELXT - integrated space-group and crystal-structure determination. Acta Crystallogr Sect C Sect C Struct Chem 71:3–8. https://doi.org/10.1107/S2053229614026370

22. Sheldrick GM (2015) Crystal structure refinement with SHELXL. Acta Crystallogr Sect C Struct Chem 71:3–8. https://doi.org/10.1107/S2053229614024218

23. Lainé P, Gourdon A, Launay JP (1995) Chemistry of iron with dipicolinic acid: synthesis, characterization and x-ray crystal-structure determination. Acta Crystallogr Sect A Found Crystallogr 51:10–17. https://doi.org/10.1107/S0001889894001247

24. Lu, F, Hu, L, Zhang, X, Xing, F, Li, MX (2016) Structural diversity and magnetic properties of six cobalt coordination polymers based on 2,2'-phosphino-dibenzoate ligand. Dalton Trans 45:19500–19510. https://doi.org/10.1039/c6dt04010a

25. Luo F, Hong MC, Shi Q, Liang YC, Zhao YJ, Wang RH, CaO R, Weng JB (2002) Synthesis, structure and magnetic properties of a quasi-two dimensional compound [Cu(C5H4NCOO)2]·2H2O. Transition Metal Chemistry 27:311–315. https://doi.org/10.1023/A:1014876514184

26. Oka Y, Inoue K (2004) Structures and magnetic properties of a new cobalt(II) linear trimer with phenylcinnamic acid. Chem Lett 33:402–403. https://doi.org/10.1246/cl.2004.402
27. Scaldini FM, Correa CC, Yoshida MI, Krambrock K, Machado FC (2014) 2-D coordination polymers of copper and cobalt with 3,4-pyridinedicarboxylic acid: synthesis, characterization, and crystal structures. J Coord Chem 67:2967–2982. https://doi.org/10.1080/00958972.2014.959002

28. Mohamadou A, Van Albada GA, Kooijman H, Wieczorek B, Spek AL, Reedijk J (2003) The binding mode of the ambidentate ligand dicyanamide to transition metal ions can be tuned by bisimidazoline ligands with H-bonding donor property at the rear side of the ligand. New J Chem 27:983–988. https://doi.org/10.1039/b212059c

29. Li GB, Yang QY, Pan RK, Liu SG (2018) Diverse cobalt(II) coordination polymers for water/ethanol separation and luminescence for water sensing applications. CrystEngComm. 20:3891–3897. https://doi.org/10.1039/C8CE00709H

30. Erer H, Yıldız OZ, Arici M (2015) A series of Zinc(II) 3D → 3D interpenetrated coordination polymers based on Thiophene-2,5-dicarboxylate and Bis(imidazole) derivative linkers. Cryst Growth Des 15:3201–3211. https://doi.org/10.1021/cg502276w

31. Tang L, Wang HH, Fu YH, Wang YT, Wang J, Hou X (2019) Three cobalt-based coordination polymers with tripodal carboxylate and imidazole-containing ligands: syntheses, structures, properties and DFT studies. RSC Adv 9:38902–38911. https://doi.org/10.1039/c9ra07737e

32. Wang HM, Liu HP, Chu TS, Yang YY, Hu YS, Liu WT, Ng SW (2014) A luminescent terbium coordination polymer for sensing methanol. RSC Adv 4:14035–14041. https://doi.org/10.1039/c4ra00745y

33. Safe M, Manual H (n.d.) METHANOL SAFE HANDLING MANUAL: 4 TH EDITION methanol safe handling manual-health and safety module 4 TH EDITION, 1–17. http://www.methanol.org/wp-content/uploads/2017/04/SafeHandlingManual-Health-Safety-Module-pdf

34. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, M. Hada, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery Jr JA, Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas Ó, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ (2009) Gaussian, Inc, Wallingford CT

35. Becke AD (1993) Density-functional thermochemistry. III. The role of exact exchange. J Chem Phys 98:5648–5652. https://doi.org/10.1063/1.464913

36. Olalekan TE, Ogunlaja AS, VanBrecht B, Watkins GM (2016) Spectroscopic, structural and theoretical studies of copper(II) complexes of tridentate NOS Schiff bases. J Mol Struct 1122:72–79. https://doi.org/10.1016/j.molstruc.2016.05.098

37. Ogunlaja AS, Hosten E, Tshentu ZR (2014) Dispersion of asphaltenes in petroleum with ionic liquids: evaluation of molecular interactions in the binary mixture. Ind Eng Chem Res 53:18390–18401. https://doi.org/10.1021/ie502672q

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.