



Synthesis, Structure and Spectroscopy of Clathrate Inclusion Compounds of Cobalt(II), Cadmium(II) and Zinc(II) *trans*-4-styrylpyridine Nitrates as Host with *trans*-4-styrylpyridine as Guest (2 : 1)

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Abstract. New clathrate inclusion compounds with the general formula, $MA_3X_2 \cdot 1/2G$ ($M = \text{Co(II)(1)}$, Cd(II)(2) , and Zn(II)(3) , $X = \text{NO}_3^-$ and A and $G = \textit{trans}$ -4-styrylpyridine), differing from the usual Werner clathrates, $MA_4X_2 \cdot 2G$, have been prepared and characterized by elemental and thermal analyses, IR and electronic spectroscopy and X-ray crystallography. Two representative compounds $[\text{Co(stpy)}_3(\text{NO}_3)_2] \cdot 1/2\text{stpy}$ (**1**) and $[\text{Cd(stpy)}_3(\text{NO}_3)_2] \cdot 1/2\text{stpy}$ (**2**) are investigated by single crystal X-ray diffraction. Compound (**1**) crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.966(2)$, $b = 12.802(4)$, $c = 16.063(5)$ Å, $\alpha = 83.38(3)$, $\beta = 71.30(2)$, $\gamma = 76.88(3)^\circ$, $Z = 2$. The structure is made up of discrete molecules of $[\text{Co(stpy)}_3(\text{NO}_3)_2]$. The central Co(II) is surrounded by three stpy nitrogen atoms and four oxygen atoms of two asymmetrically coordinated bidentate nitrate ligands. One of the oxygens is semicoordinated leading to a distorted octahedral geometry for Co(II). Compound (**2**) crystallizes in the monoclinic space group $P2_1/n$ with $a = 15.597(3)$, $b = 18.313(5)$, $c = 16.188(3)$ Å, $\beta = 115.998(14)^\circ$ and $Z = 4$. The structure consists of neutral molecules of $[\text{Cd(stpy)}_3(\text{NO}_3)_2]$. The geometry around Cd(II) is best described as pentagonal bipyramid with four oxygen atoms from symmetrical bidentate nitrate groups and one stpy nitrogen atom in the equatorial positions. Two other nitrogen atoms from stpy ligands occupy the axial positions. The guest stpy molecules are trapped in the centrosymmetrical cavities in lattices of both **1** and **2**. Compound **3** is found to be isomorphous with **2**. A large splitting of the symmetric and asymmetric NO_2 stretching vibrations reveals the presence of bidentate nitrate ligands. Thermogravimetric and DTA studies on the Cd(II) compound, show it to be a thermally stable inclusion compound.

Key words: *trans*-4-styrylpyridine complex, Werner-type clathrates, crystal structure, IR spectra, electronic spectra and thermal analysis.

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1. Introduction

The molecular design of host crystal lattices with large voids in the form of cages, channels, and interlayer space etc. poses a great challenge to crystal engineering. Such systems may trap stereoselectively guest molecules ranging from noble gases to aromatic compounds leading to stable inclusion compounds. Studies on inclusion compounds [1–3] are of current interest in understanding guest-host interaction [4–6], molecular recognition chemistry [7], dynamics of guest molecules in the lattice structures [8], and separation of isomers by selective enclathration [9–13]. In contrast to organic inclusion compounds [14], only a few types of inorganic clathrates are known. The first inorganic clathrate compound, discovered accidentally and known as the Hofmann benzene clathrate [15], possesses the composition, $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$. This compound has been further modified by replacing the hexacoordinate Ni(II) with other divalent ions such as Cd(II), Cu(II) and Zn(II) etc. and the ammine with other related ligands to give Hofmann-type inclusion compounds [1, 2]. The square planar $\text{Ni}(\text{CN})_4^{2-}$ has also been replaced by tetrahedral $\text{Zn}(\text{CN})_4^{2-}$, $\text{Cd}(\text{CN})_4^{2-}$ or $\text{Hg}(\text{CN})_4^{2-}$ resulting in what are known as Hofmann-Td-type clathrates [2]. The ability of Werner complexes to include a variety of organic guest molecules leads to the other series of inorganic clathrates known as Werner clathrates [3]. While Hofmann clathrates are represented by the general formula, $[\text{M}(\text{NH}_3)_2\text{M}'(\text{CN})_4] \cdot 2\text{G}$, the Werner clathrates have the stoichiometry, $\text{MX}_2\text{A}_4 \cdot 2\text{G}$ where $\text{M} = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}, \text{Cd}, \text{Mn}$ or Hg ; $\text{M}' = \text{Ni}, \text{Pd}$ or Pt ; $\text{G} = \text{benzene}, \text{pyrrole}, \text{thiophene}, \text{dioxane}, \text{aniline}$ or biphenyl ; $\text{X} = \text{NCS}^-, \text{NCO}^-, \text{NO}_3^-, \text{NO}_2^-, \text{Cl}^-, \text{Br}^-$ or I^- and $\text{A} = \text{pyridine}$ and 4-methylpyridine . Replacement of pyridine with bulky ligands in the Werner clathrates may enlarge as well as fine-tune the dimension of the voids in the host lattices so as to enclose selectively suitable guest molecules. Based on the strategy, an attempt has been made to substitute pyridine with *trans*-4-styrylpyridine (stpy), a pyridine derivative with a bulky styryl group in the γ -position, in the Werner clathrates and thus to develop novel host structures. Such an attempt in the present work leads to the formation of inclusion compounds with the stoichiometry, $\text{MX}_2\text{A}_3 \cdot 1/2\text{G}$ ($\text{M} = \text{Co}(\text{II}), \text{Cd}(\text{II}),$ and $\text{Zn}(\text{II}), \text{X} = \text{NO}_3^-$ and A and $\text{G} = \text{stpy}$) which differs from the composition of Werner clathrates *viz.*, $\text{MX}_2\text{A}_4 \cdot 2\text{G}$. We report here the synthesis, structure and spectral characterization of these new Werner type clathrate inclusion compounds.

2. Experimental

2.1. MATERIALS AND REAGENTS

All chemicals used were of analytical grade obtained from Aldrich, USA and Ranbaxy, India. The ligand *trans*-4-styrylpyridine was prepared according to the literature method [16, 17] and characterized by IR and ^1H NMR spectroscopy.

2.2. PHYSICAL MEASUREMENTS

Infrared spectra were recorded in the range 4000–300 cm^{-1} , as KBr pellets on a Perkin-Elmer 783 spectrophotometer using polystyrene film as a calibrant. Electronic spectra at 25 °C were recorded on a Hitachi Model 200 spectrophotometer. Microanalyses (C, H, N) were carried out by the Microanalytical Laboratory, Regional Sophisticated Instrumentation Center, Panjab University, Chandigarh, India. Metal estimations were performed using EDTA titrations [18]. TGA/DTA studies were carried out with a Stanton Redcroft, UK, Simultaneous Thermal Analyser-780.

2.3. SYNTHESIS OF $[\text{Co}(\text{stpy})_3(\text{NO}_3)_2] \cdot 1/2 \text{ stpy}$ (**1**)

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.058 g, 0.2 mmol) was added to a solution of stpy (0.217 g, 1.2 mmol) in 20 mL of methanol-ethanol (3 : 1) mixture. The resulting solution was allowed to evaporate at room temperature. Reddish-brown crystals suitable for X-ray diffraction were obtained within 2 to 3 days (yield: 0.122 g, 75%). IR data (ν/cm^{-1}): 3025 m, 3040 m, 1630 m, 1615 s, 1590 m, 1570 m, 1495 m, 1450 s (br), 1387 s, 1310 s (br), 1244 m, 1220 m, 1190 m, 1067 m, 1035 m, 1021 s, 975 m (br), 865 m, 815 s, 750 s, 725 m, 685 s, 645 m, 610 w, 540 s, 500 w, 460 w, 390 w.

2.4. SYNTHESIS OF $[\text{Cd}(\text{stpy})_3(\text{NO}_3)_2] \cdot 1/2 \text{ stpy}$ (**2**)

To a solution of stpy (0.217 g, 1.2 mmol) in methanol (20 mL) was added $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.069 g, 0.2 mmol). The solution was refluxed for 30 min. The precipitate formed was filtered off and the filtrate on slow evaporation yielded pale yellow crystals suitable for X-ray studies within 2–3 days (yield: 0.114 g, 65.5%). IR data (ν/cm^{-1}): 3045 m, 3085 m, 1635 m, 1613 s, 1600 m, 1565 m, 1517 m, 1450 s (br), 1395 s, 1310 s, 1255 w, 1235 m, 1207 m, 1170 w, 1075 m, 1043 m, 1027 s, 975 m (br), 873 m, 820 m (br), 765 s, 740 m, 700 s, 660 m, 620 w, 550 s, 500 w.

2.5. SYNTHESIS OF $[\text{Zn}(\text{stpy})_3(\text{NO}_3)_2] \cdot 1/2 \text{ stpy}$ (**3**)

A solution of stpy (0.217 g, 1.2 mmol) in methanol (10 mL) was added to a solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.059 g, 0.2 mmol) in methanol (10 mL) and the solution was heated for 10–15 min and set aside to evaporate slowly at ambient temperature. Crystals suitable for X-ray diffraction appeared after 2 to 3 days (yield: 0.106 g, 65.0%). IR data (ν/cm^{-1}): 3047 m, 3085 m, 1633 m, 1613 s, 1600 m, 1563 m, 1515 m, 1448 s (br), 1390 s, 1310 s, 1250 w, 1231 m, 1205 m, 1173 w, 1073 m, 1040 m, 1023 s, 974 m (br), 871 m, 820 m (br), 760 s, 660 m, 615 w, 542 s, 500 w.

Table I lists the analytical data for **1**, **2** and **3**, which were in agreement with the formula of the samples used for X-ray analysis.

Table I. Analytical data for compounds **1**, **2** and **3**

| Compound | Color | % Calcd. | | | | % Found | | | |
|--|--------|----------|------|------|-------|---------|------|------|-------|
| | | C | H | N | M | C | H | N | M |
| 1. Co(stpy) ₃ (NO ₃) ₂ · 1/2 stpy | Red | 66.83 | 4.81 | 9.42 | 7.21 | 66.71 | 4.69 | 9.39 | 7.19 |
| 2. Cd(stpy) ₃ (NO ₃) ₂ · 1/2 stpy | Yellow | 62.73 | 4.51 | 8.84 | 12.90 | 62.68 | 4.50 | 8.82 | 12.87 |
| 3. Zn(stpy) ₃ (NO ₃) ₂ · 1/2 stpy | Yellow | 66.31 | 4.77 | 9.35 | 7.93 | 66.27 | 4.72 | 9.35 | 7.97 |

2.6. CRYSTAL STRUCTURE DETERMINATIONS

Single crystals of (**1**) (dimensions $0.24 \times 0.28 \times 0.32$), (**2**) (dimensions $0.18 \times 0.23 \times 0.38$) and (**3**) (dimensions $0.20 \times 0.26 \times 0.36$) were used for X-ray diffraction measurements. Cell dimensions were determined by least-squares refinement of the measured setting angles of 25 reflections with ($10^\circ < \theta < 12^\circ$) for **1**, ($12^\circ < \theta < 18^\circ$) for **2** and ($12^\circ < \theta < 16^\circ$) for **3**. An examination of cell dimensions revealed that the Zn(II) compound, **3**, was isomorphous with **2**. Hence, two representative compounds, **1** and **2** were selected for full structure determination. The intensity data were collected at 293(2) K on an Enraf-Nonius CAD-4 four-circle diffractometer using graphite-monochromatized Mo-K α radiation by the ω - 2θ scan technique. A total of 7525 unique data were collected for **1** and 7570 unique data for **2**. Of these 7110 for **1** and 7288 for **2** were considered to be observed with $I > 2\sigma(I)$. Intensity data were corrected for Lorentz, polarization and absorption effects (ψ scan). Neutral atomic scattering factors were taken from reference [19]. The structures were solved by direct methods using SHELXS-86 [20] and refined on F^2 using least-squares full matrix methods implemented in SHELXL-93 [21]. All non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms were subjected to isotropic refinement. Since the complexes are crystallographically pseudo-centric, both acentric and centric space groups were tried to solve the structures. Table II lists the R , wR_2 and shift/esd values obtained for centric and acentric space groups. It is evident that the structures were not stable in acentric space groups and also the bonding parameters had greater estimated standard deviations. In centric space groups with 50 : 50 occupancy for the pyridyl nitrogen/phenyl carbon of the half molecule of stpy which exists as guest, the structures converged to an acceptable level. The results presented here are based on this model. All pertinent crystallographic data for [Co(stpy)₃(NO₃)₂] · 1/2stpy (**1**), [Cd(stpy)₃(NO₃)₂] · 1/2 stpy (**2**) and [Zn(stpy)₃(NO₃)₂] · 1/2stpy (**3**) are collected in Table III.

Table II. Details of structure refinement data obtained using different models

| Complex | Model | R_1 | wR_2 | Shift/esd max. | Largest diff. peak |
|----------|------------------------------------|--------|--------|-------------------|-----------------------|
| 1 | $P\bar{1}$ (No. 2) (C/N: 50/50) | 0.0613 | 0.1399 | 0.000 | 0.449 |
| | $P\bar{1}$ (Carbon only) | 0.0603 | 0.1359 | -0.060 | 0.444 |
| | $P1$ | 0.0507 | 0.1090 | 0.681 | 0.314 |
| 2 | $P2_1/n$ (C/N: 50/50) | 0.0430 | 0.0883 | 0.004 | 0.439 |
| | $P2_1/n$ (Carbon only) | 0.0423 | 0.0831 | 0.573 | 0.420 |
| | $P2_1$ | 0.0347 | 0.0693 | 1.126 | 0.381 |

3. Results and Discussion

3.1. CRYSTAL STRUCTURE OF $[\text{Co}(\text{stpy})_3(\text{NO}_3)_2] \cdot 1/2\text{stpy}$ (**1**)

The crystal structure of **1** consists of neutral monomeric molecules of $[\text{Co}(\text{stpy})_3(\text{NO}_3)_2]$. Figure 1 show the ORTEP diagrams of the host molecules, $[\text{Co}(\text{stpy})_3(\text{NO}_3)_2]$ ($M = \text{Co}$ and Cd) with atomic labelling scheme respectively. Selected bond lengths and angles are given in Table IV. The central Co(II) ion is coordinated by three stpy ligands through the nitrogen atom and two nitrate ligands through four oxygen atoms. Among the two nitrate groups, one is almost bonded in a bidentate fashion and the other being highly asymmetrically coordinated, resulting in the elongation of one of the Co–O(3) bonds (2.537(4) Å). The Co–O(3) distance lies in the region of semicoordination and thus the oxygen O(3) forms a semibond to the central Co(II). If this semibond is ignored, the coordination geometry about the central Co(II) atom may best be described as distorted octahedron. The equatorial positions are approximately occupied by three stpy nitrogen atoms, N(1), N(2), N(3) and an oxygen atom, O(4) from a bidentate nitrate group. The other oxygen atom, O(6) of the bidentate nitrate and an oxygen atom, O(2) from an unsymmetrically coordinated bidentate nitrate (anisobidentate mode) occupy the axial positions. The Co–O bond distances of bidentate nitrate ligand [Co–O(4) 2.323(4), Co–O(6) 2.162(3) Å] reveal that the nitrate group is asymmetrically coordinated. The asymmetry of the other nitrate group is so high that it becomes an anisobidentate ligand. It occurs, probably to minimise the steric interactions owing to the bulky stpy ligand. The bidentate coordination of the nitrate group imposes a small (4)O–Co–O(6) bond angle of about 56.05(12)°. As a consequence, the other bond angles around Co(II) show significant deviations (Table IV) from the values expected for ideal octahedral geometry.

Table III. Crystal data, intensity-data collection and structure refinement parameters

| | 1 | 2 |
|--|---|---|
| Formula | C _{45.5} H ₃₉ CoN _{5.5} O ₆ | C _{45.5} H ₃₉ CdN _{5.5} O ₆ |
| Color | red | yellow |
| <i>M</i> | 817.75 | 871.22 |
| Crystal size/mm | 0.24 × 0.28 × 0.32 | 0.18 × 0.23 × 0.38 |
| Crystal symmetry | Triclinic | Monoclinic |
| Space group | <i>P</i> $\bar{1}$ | <i>P</i> 2 ₁ /n |
| T/K | 293(2) | 293(2) |
| <i>a</i> /Å | 10.696(2) | 15.597(3) |
| <i>b</i> /Å | 12.802(4) | 18.313(5) |
| <i>c</i> /Å | 16.063(5) | 16.188(3) |
| α /° | 83.38(3) | 90 |
| β /° | 71.30(2) | 115.99(14) |
| γ /° | 76.88(3) | 90 |
| Cell volume/Å ³ | 2026.9(10) | 4156(2) |
| Formula units/unit cell | 2 | 4 |
| <i>D</i> _{calc} /g cm ⁻³ | 1.340 | 1.392 |
| μ _{calc} /mm ⁻¹ | 0.480 | 0.580 |
| Radiation used | MoK α (λ = 0.71073) | MoK α (λ = 0.71073) |
| θ Range/° | 2.05–24.98° | 2.22–24.98° |
| <i>hkl</i> ranges | –11 to 12, –14 to 15, 0 to 19 | –18 to 16, 0 to 21, 0 to 19 |
| <i>F</i> (000) | 851 | 1786 |
| Independent reflections (<i>R</i> _{int}) | 3781 | 5172 |
| Data, restraints, parameters | 7110, 0, 538 | 7284, 0, 523 |
| Goodness of fit on <i>F</i> ² | 1.002 | 1.107 |
| <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)] | 0.0613, 0.1399 | 0.0430, 0.0883 |
| <i>R</i> ₁ , <i>wR</i> ₂ (for all data) | 0.1416, 0.1638 | 0.0751, 0.1116 |
| Weighting factors <i>a</i> , <i>b</i> ^a | 0.0885, 0.0000 | 0.0364, 4.6095 |
| Largest difference peak, hole/e Å ⁻³ | 0.449, –0.433 | 0.439, –0.537 |

^a Weighting scheme $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

The (4)O–N–O(6) bond angle, 114.8°, close to the strongest Co–O interaction, is smaller than the other O–N–O bond angles, 122.6° (average), in the nitrate ligand. Further, the terminal N–O bond [N–O(5) 1.212(5) Å] is slightly shorter than the N–O bond adjacent to the strongest metal-oxygen interaction [N–O 1.254 Å], showing a discernible polarisation effect. Both the nitrate groups are planar. The Co(II) ion lies in the plane of each nitrate group. The value of 105.5(3)° for the angle Co–O(2)–N(4) is significantly less than the expected value of 110° for normal unidentate coordination [22]. This suggests the nitrate group to be aniso-

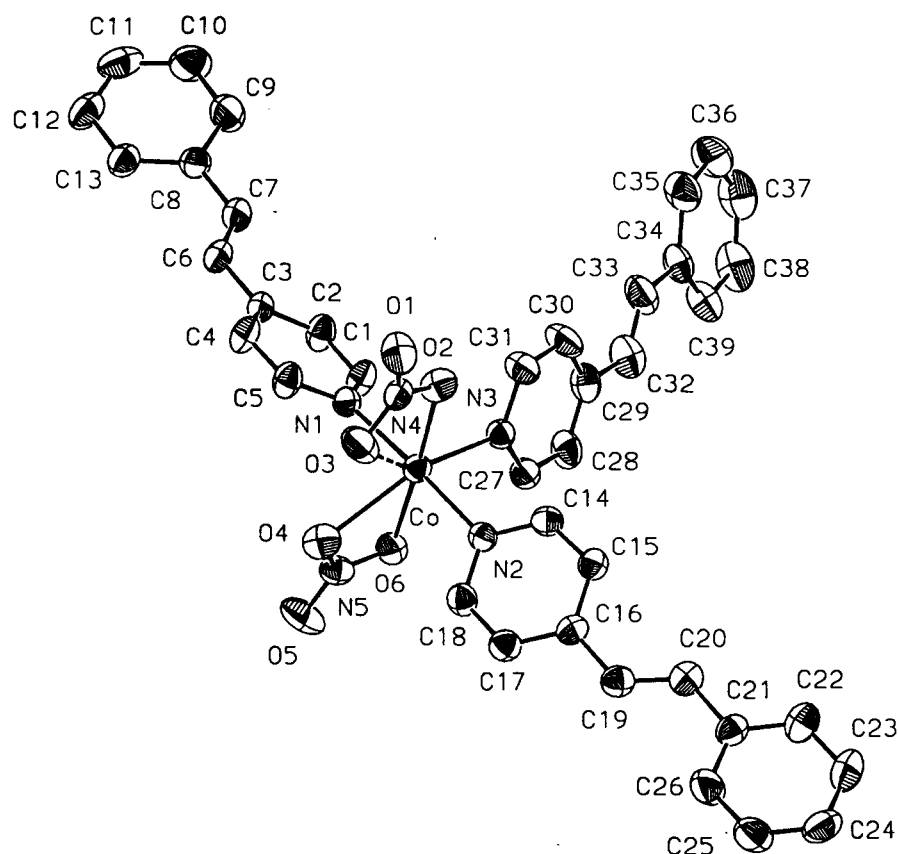


Figure 1. ORTEP representation of the host molecule, $[\text{Co}(\text{stpy})_3(\text{NO}_3)_2]$ (**1**) with atomic labelling scheme (thermal ellipsoids are drawn at 30% probability level).

bidentate. Unique bond distances and angles along with the related compounds for comparison listed in Table V are in good agreement with each other.

A unique feature is that the crystal lattice consists of stpy molecules trapped in the cavities formed between two complex moieties. The unit cell contains one additional molecule of uncoordinated free stpy on the general position with 50 : 50 occupancy for pyridyl nitrogen and phenyl carbon of the enclathrated stpy molecule. This behaviour is in contrast to the pyridine analog [23], $[\text{Co}(\text{py})_3(\text{NO}_3)_2]$, which does not exhibit inclusion ability. The Werner complex [3], $[\text{Co}(\text{py})_4(\text{NCS})_2]$ where pyridine rings of the adjacent molecules are parallel and the molecular packing is so close that no space is left available for guest molecules, also does not show any inclusion behaviour. However, $[\text{Co}(4\text{-pic})_4(\text{NCS})_2]$ (4-pic = 4-methylpyridine) is found to exhibit inclusion ability [3]. Similarly, in the present investigation, replacement of pyridine with bulky *trans*-4-styrylpyridine in $[\text{Co}(\text{py})_3(\text{NO}_3)_2]$ results in a slightly different coordination geometry and lattice structure with large voids. Each pair of molecules, which are centrosymmetrically related, form a layer-type

Table IV. Selected bond distances (Å) and bond angles (°) for $[\text{Co}(\text{stpy})_3(\text{NO}_3)_2] \cdot 1/2\text{stpy}$ (**1**)

| Bond lengths (Å) | | | |
|------------------|------------|----------------|------------|
| Co–N(1) | 2.148(3) | O(1)–N(4) | 1.216(4) |
| Co–N(2) | 2.105(3) | O(2)–N(4) | 1.263(4) |
| Co–N(3) | 2.133(3) | O(3)–N(4) | 1.221(5) |
| Co–O(2) | 2.115(3) | O(4)–N(5) | 1.243(5) |
| Co–O(4) | 2.323(4) | O(5)–N(5) | 1.207(5) |
| Co–O(6) | 2.162(3) | O(6)–N(5) | 1.265(5) |
| Co \cdots O(3) | 2.537(4) | | |
| Bond angles (°) | | | |
| N(1)–Co–N(2) | 177.46(14) | O(2)–Co–O(4) | 124.05(13) |
| N(1)–Co–N(3) | 90.83(13) | O(2)–Co–O(6) | 176.22(11) |
| N(1)–Co–O(2) | 89.54(13) | O(4)–Co–O(6) | 56.05(12) |
| N(1)–Co–O(4) | 83.88(12) | N(4)–O(2)–Co | 105.5(3) |
| N(1)–Co–O(6) | 86.72(13) | N(5)–O(4)–Co | 91.0(3) |
| N(2)–Co–N(3) | 91.41(13) | N(5)–O(6)–Co | 98.1(3) |
| N(2)–Co–O(2) | 91.71(13) | O(1)–N(4)–O(3) | 124.3(4) |
| N(2)–Co–O(4) | 93.58(12) | O(1)–N(4)–O(2) | 120.0(4) |
| N(2)–Co–N(6) | 92.05(13) | O(3)–N(4)–O(2) | 115.7(4) |
| N(3)–Co–O(2) | 88.88(14) | O(5)–N(5)–O(4) | 123.7(5) |
| N(3)–Co–O(4) | 146.45(14) | O(5)–N(5)–O(6) | 121.5(5) |
| N(3)–Co–O(6) | 90.65(14) | O(4)–N(5)–O(6) | 114.8(4) |

structure as illustrated in Figure 2. One of the stpy ligands from each molecule, which protrudes into the space between these layers, gives rise to two-dimensional cavities. These cavities, which possess a centre of symmetry, are occupied by the uncomplexed stpy.

3.2. CRYSTAL STRUCTURE OF $[\text{Cd}(\text{stpy})_3(\text{NO}_3)_2] \cdot 1/2 \text{stpy}$ (**2**)

The structure of **2** consists of monomeric neutral molecules of $[\text{Cd}(\text{stpy})_3(\text{NO}_3)_2]$. The ORTEP diagram of the host complex with atomic numbering scheme is shown in Figure 3. Selected bond distances and angles are collected in Table VI. Cd(II) is surrounded by three stpy nitrogen atoms in a T-shaped fashion and four oxygen atoms from the two nearly symmetrical bidentate nitrate groups. The geometry about Cd(II) is best described as pentagonal bipyramid with the equatorial positions occupied by one stpy nitrogen atom, N(2) and four oxygen atoms, O(1), O(2), O(4), and O(5) of the two bidentate nitrate ligands. Two other stpy nitrogen atoms, N(1)

Table V. Comparison of unique bond distances (Å) and angles (°) in $\text{Co}(\text{stpy})_3(\text{NO}_3)_2 \cdot 1/2\text{stpy}$ (1) and $[\text{Cd}(\text{stpy})_3(\text{NO}_3)_2] \cdot 1/2\text{stpy}$ (2) with related compounds

| Compound | M–N (Å) | M–O (Å) | N–O (Å) | N–O _{ter} (Å) | M–O–N (°) | O–M–O (°) |
|--|------------|------------|------------|---------------------------|--------------|--------------|
| $[\text{Co}(\text{stpy})_3(\text{NO}_3)_2] \cdot 1/2\text{stpy}^{\text{a}}$ | 2.129 | 2.243 | 1.254 | 1.207 | 94.6 | 56.05 |
| | 2.129 | 2.326 | 1.242 | 1.216 | 105.5 | 56.8 |
| $[\text{Co}(\text{py})_3(\text{NO}_3)_2]^{\text{b}}$ | 2.138 | 2.259 | 1.250 | 1.223 | 94.8 | 52.8 |
| $[\text{Co}(\text{C}_4\text{H}_6\text{N}_2)_4(\text{NO}_3)]\text{NO}_3^{\text{c}}$ | 2.132 | 2.192 | 1.200 | 1.230 | – | 56.8 |
| $[\text{Cd}(\text{stpy})_3(\text{NO}_3)_2] \cdot 1/2\text{stpy}^{\text{a}}$ | 2.311 | 2.459 | 1.256 | 1.221 | 95.5 | 51.7 |
| $[\text{Cd}(\text{py})_3(\text{NO}_3)_2]^{\text{d}}$ | 2.324 | 2.468 | 1.262 | 1.213 | 96.3 | 51.3 |
| $[\text{Cd L}(\text{NO}_3)_2]^{\text{e}}$ | 2.412 | 2.425 | 1.258 | 1.225 | 94.8 | 52.3 |
| $[\text{Cd L}^1(\text{NO}_3)_2]^{\text{f}}$ | 2.258 | 2.482 | 1.237 | 1.216 | 96.5 | 50.1 |
| $[\text{Cd L}^2(\text{NO}_3)_2]^{\text{f}}$ | 2.335 | 2.475 | 1.246 | 1.225 | 96.5 | 56.6 |
| $[\text{Cd L}^3(\text{NO}_3)_2]^{\text{g}}$ | 2.277 | 2.428 | 1.266 | 1.207 | 95.3 | 52.3 |
| $[\text{Cd L}^4(\text{NO}_3)_2]^{\text{g}}$ | 2.308 | 2.457 | 1.255 | 1.223 | 95.4 | 51.5 |

L = (3,5-dimethylpyrazol-1-ylmethyl)amine; L¹ = 1,4,7,10-tetraoxa-13-azacyclopentadecane; L² = 1,4,7,10,13-pentaoxa-16-azacyclooctadecane; L³ = [2-(3,5-dimethyl-1-pyrazolyl)ethyl]oxide; L⁴ = [2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine.

^a This work.

^b Taken from Ref. [23].

^c Taken from Ref. [24].

^d Taken from Ref. [25].

^e Taken from Ref. [26].

^f Taken from Ref. [27].

^g Taken from Ref. [28].

and N(3), occupy the axial positions. The Cd–O bond distances [Cd–O(1) 2.478(3), Cd–O(2) 2.428(3), Cd–O(4) 2.434(3), Cd–O(5) 2.494(3) Å] indicate that both the nitrate groups are almost symmetrically bidentate. The very small bite angles, O(1)–Cd–O(2) 52.08° (11) and O(4)–Cd–O(5) 51.34(12)° compared to the Co(II) analog, O(4)–Co–O(6) 56.05(12)°, also suggest relatively symmetrical bidentate coordination of the nitrate ligands. The O–N–O bond angle, 117.25° (average) close to the strongest Cd–O is only slightly smaller than the other O–N–O bond angles of the nitrate ligands, [121.38° (average)]. The N–O bond distances adjacent to the strongest metal-oxygen interaction [N–O 1.256 Å] are slightly longer than the terminal N–O bond distance (1.221 Å) indicating a small polarization effect. The cadmium atom is present (0.048(2) Å) above the plane formed by the atoms Cd, N(5), O(4), O(5), O(6) and 0.076(1) Å (above for the plane comprising the atoms Cd, N(4), O(1), O(2), O(3)). This reveals that, upon metal coordination, there is no significant change in the geometry of the nitrate ions. Cd(II) is 0.026 Å away from the plane defined by the three N(stpy) atoms while Co(II) deviates only by 0.015 Å. This results in greater access to the Cd(II) ion and allows for a bident-

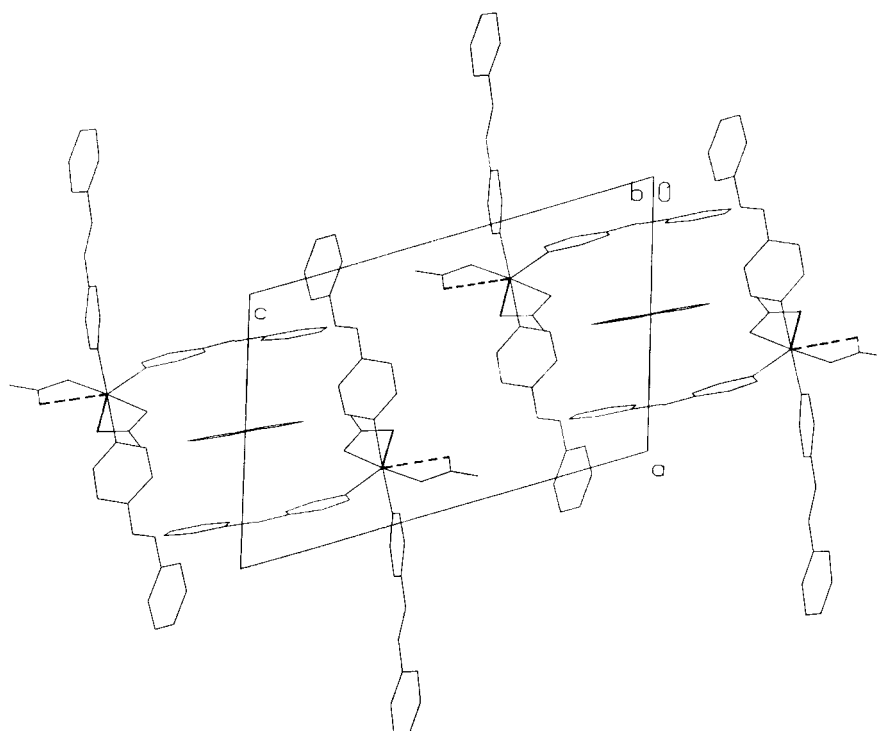


Figure 2. Perspective view of the crystal structure of **1**, showing centro-symmetrical voids occupied by uncomplexed stpy molecules, viewed along the *b* axis.

ate coordination of nitrate, leading to regular seven-coordination around Cd(II). The Cd–O–N bond angle, 95.3° , agrees well with the values normally expected for metal-nitrato symmetric bidentate coordination [25]. Selected bond distances and angles along with the related compounds for comparison listed in Table V are shown to be in good agreement with each other. The overall molecular geometry around Cd(II) is similar to the pyridine analog, $[\text{Cd}(\text{py})_3(\text{NO}_3)_2]$. However, akin to the Co(II) analog (**1**), the lattice structure of $[\text{Cd}(\text{stpy})_3(\text{NO}_3)_2]$ contains large centrosymmetric voids, which are occupied by the free stpy molecules. Here, one set of pair of centrosymmetrically related molecules form a layer, which is divided into cavities by the coordinated stpy molecule. Another pair of host molecules form a layer, which are however, twisted by about 176.9° , leading to a rather two-dimensional interconnection to a one-dimensional channel (Figure 4).

In contrast to the Co(II)(**1**) and Cd(II)(**2**) compounds, our recent study revealed that the Cu(II) analog [29], $[\text{Cu}(\text{stpy})_4(\text{ONO}_2)(\text{ONO}_2)']$ possesses a distorted octahedral geometry showing no inclusion behaviour. This marked difference in coordination geometry and lattice structure from their Co(II), Zn(II) and Cd(II) analogs probably arises due to the smaller size and plasticity effect of Cu(II). Thus, the degree of asymmetry of the nitrate groups increases with decreasing metal ionic

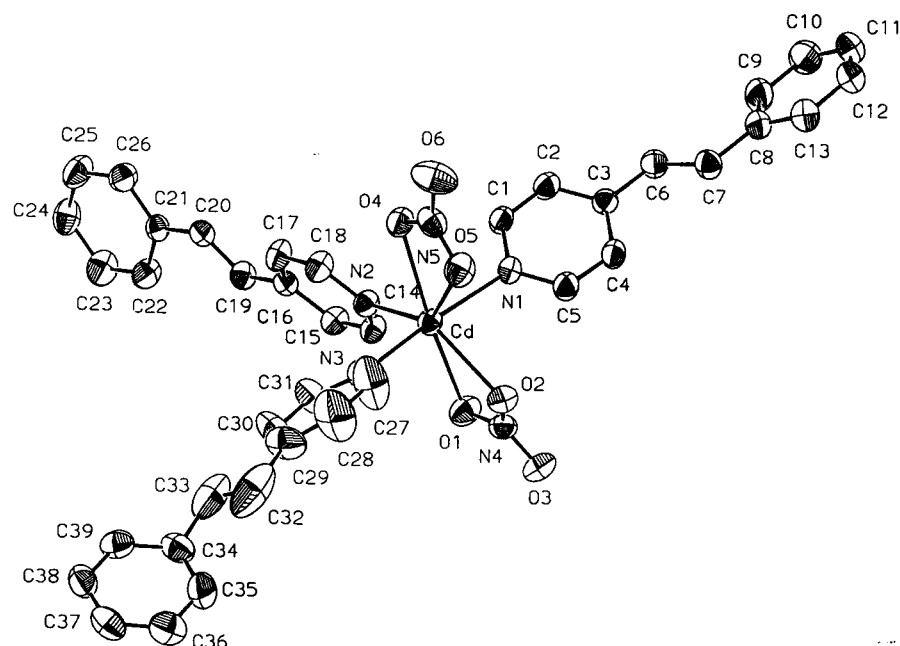


Figure 3. ORTEP diagram of host molecule, $[\text{Cd}(\text{stpy})_3(\text{NO}_3)_2]$ (**2**) with atomic numbering scheme (thermal ellipsoids are drawn at 30% probability level).

radius and in other words, the tendency for seven coordination increases in the order $\text{Cu}(\text{II}) < \text{Co}(\text{II}) \ll \text{Cd}(\text{II})$.

3.3. COMPARISON OF COORDINATED STPY WITH GUEST STPY

The dihedral angles of the *trans*-configuration in coordinated and guest stpy molecules are as follows.

| Moiety | 1 | 2 |
|----------------------------------|--------------------|--------------------|
| Stpy 1 (C(3)–C(6)–C(7)–C(8)) | 179.9(4) $^\circ$ | 177.3(5) $^\circ$ |
| Stpy 2 (C(16)–C(19)–C(20)–C(21)) | –179.1(4) $^\circ$ | –175.2(4) $^\circ$ |
| Stpy 3 (C(29)–C(32)–C(33)–C(34)) | –174.7(5) $^\circ$ | 177.8(4) $^\circ$ |
| Guest stpy | 180.0 $^\circ$ | 180.0 $^\circ$ |

The values are close to the expected 180 $^\circ$. Thus, no significant change in the *trans*-configuration of the stpy ligand occurs upon coordination/enclathration. Also, it suggests the absence of any lattice strain on it in the crystal. The thermal parameters of the guest stpy are not significantly different from the atoms of coordinated stpy. This indicates that the guest molecules are also tightly held in the lattice as revealed in thermal analysis by the simultaneous release of both coordinated and free stpy

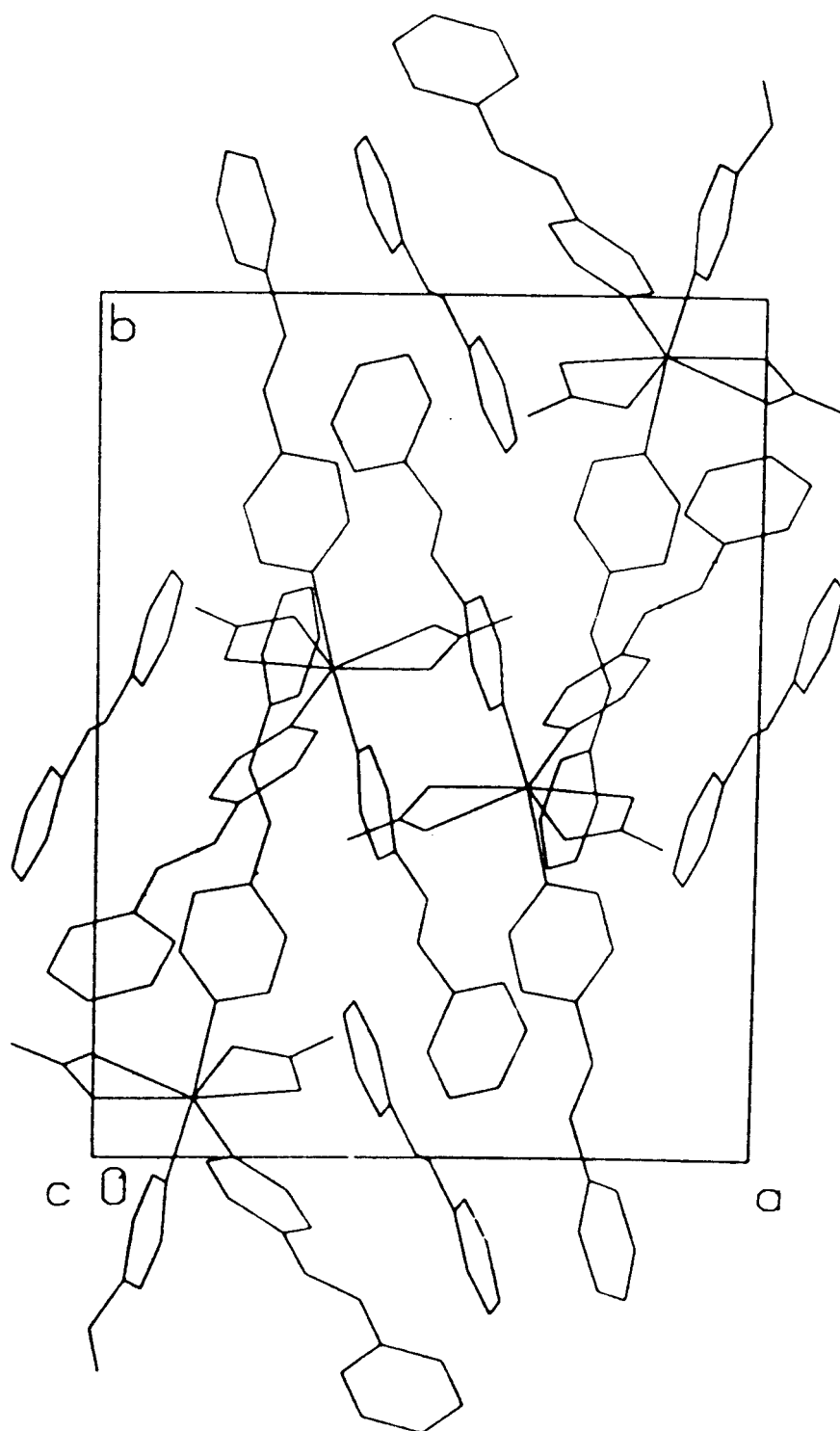


Figure 4. Projection of the crystal structure of **2**, showing centrosymmetrical voids occupied by free stpy molecules, viewed along the *c* axis.

Table VI. Selected bond distances (Å) and bond angles (°) for [Cd(stpy)₃(NO₃)₂] · 1/2stpy (**2**)

| Bond lengths (Å) | | | |
|------------------|------------|----------------|------------|
| Cd–N(1) | 2.313(3) | O(1)–N(4) | 1.256(5) |
| Cd–N(2) | 2.321(3) | O(2)–N(4) | 1.261(4) |
| Cd–N(3) | 2.299(4) | O(3)–N(4) | 1.222(5) |
| Cd–O(1) | 2.478(3) | O(4)–N(5) | 1.260(5) |
| Cd–O(2) | 2.428(3) | O(5)–N(5) | 1.247(5) |
| Cd–O(4) | 2.434(3) | O(6)–N(5) | 1.219(5) |
| Cd–O(5) | 2.494(3) | | |
| Bond angles (°) | | | |
| N(1)–Cd–N(2) | 94.69(12) | N(3)–Cd–O(5) | 86.43(14) |
| N(1)–Cd–N(3) | 168.74(14) | O(1)–Cd–O(2) | 52.08(11) |
| N(1)–Cd–O(2) | 86.35(12) | O(1)–Cd–O(4) | 166.52(11) |
| N(1)–Cd–O(4) | 83.88(12) | O(1)–Cd–O(5) | 136.79(12) |
| N(1)–Cd–O(1) | 86.48(12) | O(2)–Cd–O(4) | 136.21(11) |
| N(2)–Cd–N(3) | 96.38(14) | O(2)–Cd–O(5) | 85.25(12) |
| N(2)–Cd–O(2) | 137.33(11) | O(4)–Cd–O(5) | 51.34(12) |
| N(2)–Cd–O(4) | 86.07(11) | O(1)–N(4)–O(2) | 117.7(4) |
| N(2)–Cd–O(1) | 85.35(12) | O(3)–N(4)–O(2) | 121.0(4) |
| N(3)–Cd–O(2) | 86.88(13) | O(3)–N(4)–O(1) | 121.3(4) |
| N(3)–Cd–O(4) | 94.85(13) | O(6)–N(5)–O(5) | 123.1(5) |
| N(3)–Cd–O(1) | 96.42(14) | O(4)–N(5)–O(6) | 120.1(5) |
| N(1)–Cd–O(5) | 84.05(12) | O(5)–N(5)–O(4) | 116.8(4) |
| N(2)–Cd–O(5) | 137.36(11) | N(4)–O(1)–Cd | 93.7(3) |
| N(4)–O(2)–Cd | 95.9(2) | N(5)–O(4)–Cd | 97.0(3) |
| N(5)–O(5)–Cd | 94.5(3) | | |

from the lattice. The dihedral angles of the pyridyl and phenyl rings of stpy in **1** and **2** are as follows

- 1** 35.7° (stpy 1), 17.7° (stpy 2), and 24.3° (stpy 3)
- 2** 27.4° (stpy 1), 19.8° (stpy 2), and 34.9° (stpy 3)

This indicates the conformational flexibility of the pyridyl and phenyl rings of stpy. The crystal packing is largely achieved by normal van der Waals contacts.

3.4. SPECTROSCOPIC PROPERTIES

The tentative assignments of selected IR bands for the free ligand, stpy and its complexes **1**, **2** and **3** are given in Table VII. It is evident that the IR spectra of the inclusion complexes of Cd(II) and Zn(II) with stpy are similar, which agrees well with the structural isomorphism based on the X-ray data. All the three complexes exhibit strong bands at *ca.* 1450 and 1310 cm^{-1} , which are assigned to symmetric (ν_4) and asymmetric (ν_1) NO_2 stretching vibrations of nitrate ligands respectively. The separations of these bands ($\nu_4 - \nu_1 = 140 \text{ cm}^{-1}$) are in the range noted for bidentate coordination [30] of nitrate groups. These bands are split in **1** but present as rather sharp bands in **2** and **3**, and are perhaps due to the asymmetrical coordination of the chelate nitrate anions as revealed by X-ray data. The $\nu(\text{C}=\text{N})$ band is shifted to higher frequencies by *ca.* 30 cm^{-1} in these complexes compared with that of free stpy. It confirms the coordination of stpy through the nitrogen atom. The bands in the regions 1630 and 980 cm^{-1} are assigned to the $\nu_{(-\text{C}=\text{C}-)}$ stretching and $\delta_{(\text{C}-\text{H})}$ out of plane bending modes of the *trans*-configuration of stpy respectively. Insignificant differences in these bands between the free ligand and the complexes reveal the absence of change in the *trans*-configuration upon coordination. They further show two bands in the region *ca.* 650 and 610 cm^{-1} resulting from the presence of free uncoordinated stpy ligand in the lattices in agreement with X-ray data [31, 32].

The electronic spectra of **1** were recorded in methanol solution and Nujol mull. The approximately similar shapes and positions of the absorption bands indicate no appreciable change in the stereochemistry of the complex in solution. Broad absorption bands at $\sim 507 \text{ nm}$ and shoulders at $\sim 470 \text{ nm}$, are similar to the pyridine analog [32], $[\text{Co}(\text{py})_3(\text{NO}_3)_2]$. These features reveal that the immediate environment around Co(II) ions deviates from a regular octahedral geometry, in agreement with the X-ray data. The ligand-field parameters, calculated from the positions of the absorption bands, $Dq = 968 \text{ cm}^{-1}$, and interelectronic repulsion parameter, ' B' ' = 857 cm^{-1} , lie in the range expected for an octahedral environment. The reduction in the B value compared to the free ion indicates the bonding to be fairly covalent in **1**. Co(II), being a d^7 ion, has an excited state susceptible to Jahn–Teller distortion. The two bands observed are the bands due to the spin allowed transition from the $^4\text{T}_{1g}(\text{F})$ ground state to the excited quartet states, $^4\text{A}_{2g}$ and $^4\text{T}_{1g}(\text{P})$ which arise from JT splitting [33].

3.5. THERMAL ANALYSIS

TGA/DTA on representative compound **2** reveals it to be stable upto 170°C in contrast to the pyridine analogs, $[\text{Cu}(\text{py})_4(\text{NO}_3)_2] \cdot 2\text{py}$ [34] and $[\text{Zn}(\text{py})_4(\text{NO}_3)_2] \cdot 2\text{py}$ [35], which decompose rather readily. Generally, inclusion compounds have been classified either as thermally unstable or stable compounds [3]. The thermally unstable compounds dissociate into host and guest before the actual thermal decomposition of the host begins. On the other hand in the stable inclusion com-

Table VII. Selected IR spectral data^a for **1**, **2** and **3** along with free stpy ligand for comparison

| Stpy | 1 | 2 | 3 | Assignment |
|---------------|--------------------|--------------------|--------------------|---|
| 3051 s | 3050 w | 3055 w | 3055 w | $\nu_{\text{C-H}}$ |
| 1588 s | 1605 s | 1620 s | 1620 s | ν (ring vibration) |
| 638 m | 645 m | 652 m | 650 m | π_{inp} pyridyl ring |
| | 610 ^c w | 610 ^c w | 610 ^c w | |
| 475 m | 490 w | 500 w | 505 w | π_{op} pyridyl ring |
| 1667 m | 1665 m | 1660 m | 1660 m | $\nu_{\text{C=C}}$ (<i>trans</i> -CH=CH-) |
| 1305 s | 1308 s | 1305 s | 1305 | $\delta_{\text{C-H}}$ (<i>trans</i> -CH=CH-) |
| 970 m | 975 s | 970 s | 970 s | |
| Nitrate Bands | | | | |
| | 1450 s | 1452 s | 1452 s | $\nu_4(b_1)$ |
| | 1310 s | 1310 s | 1310 s | $\nu_1(a_1)$ |
| | 140 | 142 | 142 | $\Delta\nu(\nu_4 - \nu_1)$ |
| | 1030 m | 1035 m | 1035 m | $\nu_2(a_1)$ |
| | 810 m | 815 m | 820 m | $\nu_6(b_2)$ |
| | | | | non-planar def. |

^a as KBr pellets; op, out of plane bend; inp, in plane bend; def, deformation; ^c uncomplexed stpy; m, medium; s, strong; w, weak.

pound, escape of the guest molecule is accompanied by chemical destruction of the host. The decomposition of inclusion compound **2** proceeds by two exothermic steps. The first step occurs between 170 and 360°C. The weight loss corresponds to the loss of three and a half molecules of stpy (Found: 72.65%, Calc.: 72.71%). This simultaneous liberation of guest as well as coordinated stpy in the host lattice suggests the compound be classified as a stable inclusion compound. It reveals strong interaction between the trapped stpy molecules and the host lattice. The second weight loss occurs between 360 and 505°C corresponding to the release of nitrogen oxides (Found: 12.35%, Calc.: 12.40%). The final plateau region above 505°C corresponds to the formation of CdO (Found: 14.67%, Calc.: 14.74%).

4. Conclusion

The present investigation reveals that new clathrate inclusion compounds are obtained by the interaction of *trans*-4-styrylpyridine as ligand with $\text{M}(\text{NO}_3)_2$ having the general formula $\text{MX}_2\text{A}_3 \cdot 1/2\text{G}$ ($\text{M} = \text{Co}(\text{II}), \text{Cd}(\text{II})$ and $\text{Zn}(\text{II})$, $\text{X} = \text{NO}_3^-$ and A and $\text{G} = \text{stpy}$) different from the composition of Werner clathrates *viz.*, $\text{MX}_2\text{A}_4 \cdot 2\text{G}$, and are the first of their kind to be synthesised. $\text{Co}(\text{II})$ in compound, **1** shows a distorted octahedral stereochemistry. However, $\text{Cd}(\text{II})$, owing to its large ionic radius, leads to seven-coordination in **2** and the geometry is pentagonal bipyramid.

Replacement of pyridine with bulky *trans*-4-styrylpyridine prevents close packing resulting in large voids in their host lattices. These voids are occupied by the un-complexed stpy. Further studies on the inclusion of other organic guest molecules are in progress.

Supplementary material

Details of data collection, structure determination, atomic coordinates and equivalent isotropic displacement parameters, a complete lists of bond lengths and angles, anisotropic thermal parameters, and hydrogen atom parameters are deposited as supplementary material.

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