

Hydrogen-bonded hexagonal and pseudo-hexagonal grid motifs in supramolecular cobalt(II) and nickel(II) cupferronato complexes incorporating neutral N-donors with intermolecular NH₂ connectors and solvent molecules

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The cobalt(II) and nickel(II) cupferronato (*N*-nitroso-*N*-phenylhydroxylaminato) mixed-ligand complexes of 2-amino-pyridine (2-NH₂py) [Co(PhN₂O₂)₂(2-NH₂py)₂] (1), [Ni(PhN₂O₂)₂(2-NH₂py)₂] (2) and 2,6-diamino-4-phenyl-1,3,5-triazine (dpt) [Co(PhN₂O₂)₂(dpt)₂].[Co(PhN₂O₂)₂-(EtOH)₂] (3) have been synthesized and characterized by X-ray diffraction analysis. The cobalt (1) and nickel (2) complexes are isostructural. The crystal lattice of (3) contains different neutral cobalt(II) complexes [Co(PhN₂O₂)₂(dpt)₂] (3*a*) and [Co(PhN₂O₂)₂(EtOH)₂] (3*b*). Molecules of (1)–(3) contain octahedral metal centres with all-*cis*-(1) and -(2) and all-*trans*-(3) disposal of the ligands. Intramolecular N–H···O hydrogen bonding between the NH₂ groups and the O atom of the cupferronato anion can be observed in (1)–(3). Intermolecular N–H···O and N–H···N interactions between symmetry-related molecules of (1) and (2) led to hexameric aggregates which connect through common edges into a two-dimensional supramolecular network of hexagonal-grid type. In complex (3) the self-complementary dpt units of the (3*a*) molecules are maintained by intermolecular N–H···N hydrogen bonds, generating infinite chains. These (3*a*) chains are crosslinked by the (3*b*) subunits *via* N–H···O and O–H···N hydrogen bonds, thus completing the parallel two-dimensional supramolecular network consisting of pseudo-hexagonal-grid sheets. In each crystal structure the two-dimensional supramolecular networks are controlled by both hydrogen bonds and $\pi\cdots\pi$ stacking interactions.

1. Introduction

Efforts have been made recently in constructing predictable assemblies of coordination compounds *via* directional hydrogen bonding and metal–ligand intermolecular interactions (Subramanian & Zaworotko, 1994, and references therein; Braga *et al.*, 1998, and references therein; Haiduc & Edelman, 1999). Several strategies have been subsequently used for the crystal engineering of supramolecular assemblies constructed by the aid of hydrogen bonds (Fig. 1). Thus, the supramolecular array can be formed by hydrogen bonds:

- (i) between the functional (connector) groups of the ligands only (Burrows *et al.*, 1995; Qin *et al.*, 1999);
- (ii) between coordinated ligands and coordinated water (Carcia *et al.*, 2000; Dong *et al.*, 2000; Song *et al.*, 2000);
- (iii) between coordinated water and non-coordinated spacer molecules (Dong *et al.*, 2000; Moliner *et al.*, 1999; Shen *et al.*, 1999);

(iv) between coordinated ligands and non-coordinated water (Carcia *et al.*, 2000; Chen *et al.*, 1998; Janiak *et al.*, 1999, and references therein);

(v) between coordinated (chelating) ligands and non-coordinated spacer molecules (Burrows *et al.*, 2000; Chowdhry *et al.*, 1996; Qin *et al.*, 2000; Su *et al.*, 1998);

(vi) between coordinated water and non-coordinated water (Chen *et al.*, 1998); or

(vii) between coordinated Cl and coordinated water or NH ligand groups (Aullon *et al.*, 1998; Mareque Rivas & Brammer, 1998).

Aakeröy and co-workers (Aakeröy, 1997; Aakeröy *et al.*, 1998, 1999; Aakeröy & Leinen, 1999) have outlined the possibilities of creating infinite hydrogen-bonded one-dimensional, two-dimensional and three-dimensional metal-containing frameworks based on coordination complexes in which the specific coordination geometry propagates through the crystal structure by attaching substituents (intermolecular connectors) to the ligands. In most cases the complementary functions of the same ligands govern the self-assembly of coordination complexes *via* hydrogen-bonded interactions according to strategy (i).

To increase the complexity and dimensionality of these non-covalently assembled coordination complexes we have supplemented these strategies by using different multifunctional hydrogen-bond acceptor and donor ligands, as well as octahedral coordination geometry around metal ions. The genuine ability of the chelating *N*-nitroso-*N*-phenylhydroxylaminato anion (PhN_2O_2^- , cupferronato) acting as a multifunctional hydrogen-bond acceptor ligand (*e.g.* in several Sn^{IV} complexes, Deák *et al.*, 1999, 2000) has been tested in the formation of a *trans*- $[\text{Co}(\text{PhN}_2\text{O}_2)_2(\text{MeOH})_2]$ complex (A), in which the recrystallization medium MeOH served as the neutral donor molecule (Deák *et al.*, 1998). This compound is isostructural with the analogous nickel(II) complex (Okabe & Tamaki, 1995). The OH group of the methanol molecule acts as a single hydrogen-bond donor and forms bifurcated intermolecular $\text{O}-\text{H}\cdots\text{X}$ ($\text{X} = \text{O}, \text{N}$) hydrogen bonds with the

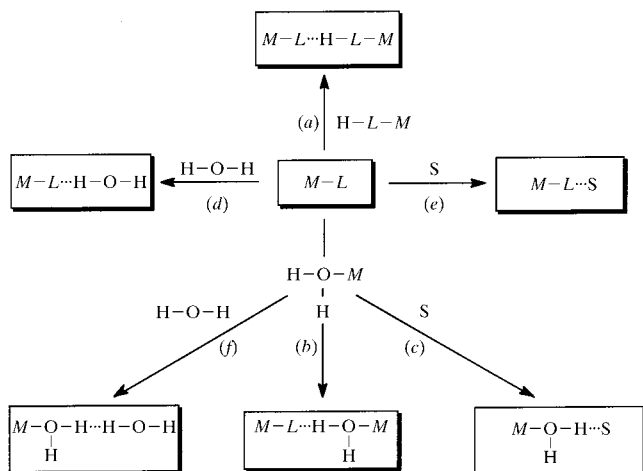


Figure 1

Schematic representation of strategies used for the crystal engineering of coordination complexes constructed by the aid of hydrogen bonds.

cupferronato O and N atoms, generating a one-dimensional network (Deák *et al.*, 1998).

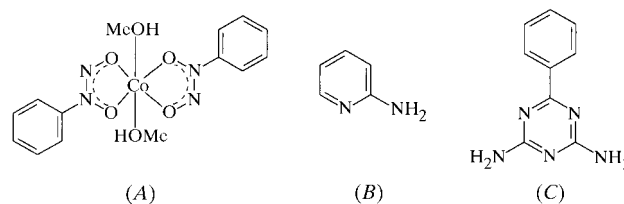
Thus, the inclusion of alcohol ROH molecules in such complexes could only generate one-dimensional chains of hydrogen-bonded molecules. In order to construct more sophisticated hydrogen-bonded networks the monofunctional MeOH was replaced by novel ligands with additional NH_2 functions acting as double donors. We have chosen 2-aminopyridine (2- NH_2py) and 2,6-diamino-4-phenyl-1,3,5-triazine (dpt) for three reasons:

(i) their known capacity to coordinate *via* the ring N atom to the metal centres,

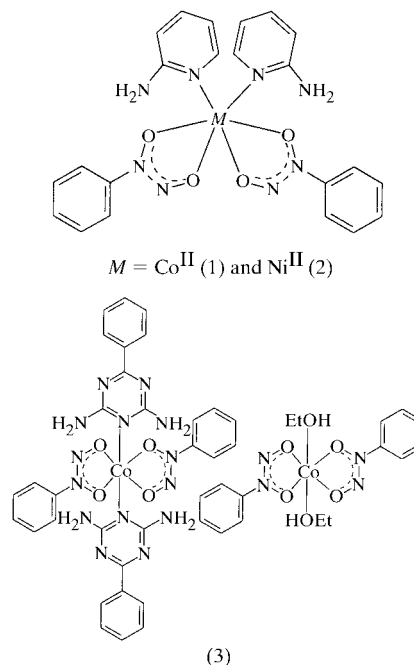
(ii) their NH_2 function acting as a double hydrogen-bond donor and

(iii) their relatively flat geometry.

The 2- NH_2py molecule (B) contains only one N atom in the ring and one NH_2 function, while the dpt molecules (C) possesses three N atoms in the ring and two NH_2 functions as potential connectors.



Herein we report the synthesis and structural characterization by single-crystal X-ray diffraction analysis of two isostructural cobalt(II) $[\text{Co}(\text{PhN}_2\text{O}_2)_2(2\text{-NH}_2\text{py})_2]$ (1) and nickel(II) $[\text{Co}(\text{PhN}_2\text{O}_2)_2(2\text{-NH}_2\text{py})_2]$ (2) complexes, and a binuclear $[\text{Co}(\text{PhN}_2\text{O}_2)_2(\text{dpt})_2] \cdot [\text{Co}(\text{PhN}_2\text{O}_2)_2(\text{EtOH})_2]$ complex (3).



These complexes (1)–(3) form two-dimensional hexagonal and pseudo-hexagonal grid networks, respectively, in the

Table 1
Experimental details.

| | (1) | (2) | (3) |
|---|--|--|--|
| Crystal data | | | |
| Chemical formula | C ₂₂ H ₂₂ CoN ₈ O ₄ | C ₂₂ H ₂₂ N ₈ NiO ₄ | C ₂₃ H ₂₅ CoN ₉ O ₅ |
| Chemical formula weight | 521.41 | 521.19 | 566.45 |
| Cell setting, space group | Monoclinic, <i>P</i> 2 ₁ / <i>n</i> | Monoclinic, <i>P</i> 2 ₁ / <i>n</i> | Triclinic, <i>P</i> $\bar{1}$ |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 8.270 (1), 11.579 (2), 25.019 (4) | 8.321 (1), 11.535 (2), 24.852 (2) | 10.225 (1), 10.214 (2), 14.163 (1) |
| α , β , γ (°) | 90, 91.42 (2), 90 | 90, 91.55 (1), 90 | 73.340 (9), 68.180 (8), 70.450 (13) |
| <i>V</i> (Å ³) | 2395.0 (6) | 2384.5 (5) | 1271.6 (3) |
| <i>Z</i> | 4 | 4 | 2 |
| <i>D</i> _x (Mg m ⁻³) | 1.446 | 1.452 | 1.479 |
| Radiation type | Mo <i>K</i> α | Mo <i>K</i> α | Mo <i>K</i> α |
| No. of reflections for cell parameters | 25 | 25 | 25 |
| θ range (°) | 14.97–16.48 | 14.30–18.38 | 14.0–14.86 |
| μ (mm ⁻¹) | 0.762 | 0.859 | 0.728 |
| Temperature (K) | 293 (2) | 293 (2) | 293 (2) |
| Crystal form, colour | Prism, red | Prism, green | Prism, dark orange |
| Crystal size (mm) | 0.45 × 0.40 × 0.40 | 0.65 × 0.40 × 0.30 | 0.50 × 0.25 × 0.25 |
| Data collection | | | |
| Diffractometer | Enraf–Nonius CAD-4 | Enraf–Nonius CAD-4 | Enraf–Nonius CAD-4 |
| Data collection method | ω -2 θ scans | ω -2 θ scans | ω -2 θ scans |
| Absorption correction | Psi-scan | Psi-scan | Psi-scan |
| <i>T</i> _{min} | 0.945 | 0.876 | 0.889 |
| <i>T</i> _{max} | 1 | 1 | 1 |
| No. of measured, independent and observed parameters | 6214, 5671, 3093 | 7525, 6888, 3620 | 23 705, 11 074, 7753 |
| Criterion for observed reflections | <i>I</i> > 2 σ (<i>I</i>) | <i>I</i> > 2 σ (<i>I</i>) | <i>I</i> > 2 σ (<i>I</i>) |
| <i>R</i> _{int} | 0.0153 | 0.0167 | 0.0130 |
| θ _{max} (°) | 27.97 | 29.97 | 34.96 |
| Range of <i>h</i> , <i>k</i> , <i>l</i> | -10 → <i>h</i> → 0 -15 → <i>k</i> → 0 -33 → <i>l</i> → 33 | 0 → <i>h</i> → 11 0 → <i>k</i> → 16 -34 → <i>l</i> → 34 | -16 → <i>h</i> → 16 -16 → <i>k</i> → 16 -22 → <i>l</i> → 22 |
| No. and frequency of standard reflections | 3 every 60 min | 3 every 60 min | 3 every 60 min |
| Intensity decay (%) | 2 | 4 | 4 |
| Refinement | | | |
| Refinement on | <i>F</i> ² | <i>F</i> ² | <i>F</i> ² |
| <i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i> | 0.0407, 0.1132, 0.962 | 0.0359, 0.0947, 0.93 | 0.036, 0.1055, 0.978 |
| No. of reflections and parameters used in refinement | 5671, 316 | 6888, 316 | 11074, 360 |
| H-atom treatment | Mixed | Mixed | Mixed |
| Weighting scheme | $w = 1/[\sigma^2(F_o^2) + (0.0635P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$ | $w = 1/[\sigma^2(F_o^2) + (0.0484P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$ | $w = 1/[\sigma^2(F_o^2) + (0.0683P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$ |
| (Δ / σ) _{max} | 0.002 | 0.001 | 0.000 |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³) | 0.322, -0.282 | 0.329, -0.268 | 0.637, -0.455 |

Computer programs used: CAD-4 EXPRESS, XCAD4 (Harms 1996), SHELXS97 (Sheldrick, 1997a), SHELXL97 (Sheldrick, 1997b).

crystal lattice, based on the mutual recognition of molecules by hydrogen-bonding interactions.

2. Experimental

2.1. Syntheses

Complex (1) was prepared by the reaction of [Co(Ph-N₂O₂)₂(H₂O)₂] with 2-aminopyridine (1:2 molar ratio) in ethanol at room temperature. After stirring for 1 h the solvent

was evaporated and the product was isolated as a microcrystalline solid. Recrystallization from methanol (or ethanol) gave the product as dark-red crystals with m.p. 426–429 K; C₂₂H₂₂N₈O₄Co: calc. C 50.7, H 4.3, N 21.5; found C 51.0, H 4.5, N 21.4%.

Complex (2) was obtained by the reaction of [Ni(Ph-N₂O₂)₂(H₂O)₂] with 2-aminopyridine (1:2 molar ratio) in ethanol at room temperature in a manner similar to complex (1). The green crystals of (2) were obtained from ethanol (m.p. 423–426 K); C₂₂H₂₂N₈O₄Ni: calc. C 50.7, H 4.3, N 21.5; found C 50.5, H 4.6, N 21.5%.

Complex (3) was prepared by the reaction of an ethanolic solution of [Co(Ph-N₂O₂)₂(H₂O)₂] with 2,6-diamino-4-phenyl-1,3,5-triazine (1:2 molar ratio) dissolved in warm ethanol. The clear red solution was stirred for 1 h at room temperature. The solvent was evaporated and the product was isolated as a microcrystalline solid. Recrystallization from ethanol gave the product as dark orange crystals (m.p. 403–405 K); C₄₆H₅₀N₁₈O₁₀Co₂: calc. C 48.8, H 4.5, N 22.3; found C 48.5, H 4.7, N 22.5%.

2.2. Data collection, structure solution and refinement

Crystal data, data collection and refinement parameters are summarized in Table 1.¹ Intensity data were collected on an Enraf–Nonius CAD-4 diffractometer (Enraf–Nonius, 1992) with graphite-monochromated

Mo *K*α radiation ($\lambda = 0.71073$ Å) using the ω -2 θ scan technique. Three standard reflections were monitored every hour; these remained constant within experimental error. The monoclinic space group *P*2₁/*n* for both (1) and (2) was uniquely assigned from the systematic absences. Compound (3) is triclinic and the space group *P* $\bar{1}$ was chosen and confirmed by the successful solution and refinement of the

¹Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE0010). Services for accessing these data are described at the back of the journal.

Table 2

Selected interatomic bond distances (Å) and bond angles (°) for (1) and (2).

| | <i>M</i> = Co (1) | | <i>M</i> = Ni (2) | |
|---|---------------------|---------------------|---------------------|---------------------|
| | <i>L</i> = <i>A</i> | <i>L</i> = <i>B</i> | <i>L</i> = <i>A</i> | <i>L</i> = <i>B</i> |
| <i>M</i> (1)—O(1 <i>L</i>) | 2.0690 (17) | 2.0708 (17) | 2.0506 (13) | 2.0481 (13) |
| <i>M</i> (1)—O(2 <i>L</i>) | 2.0992 (18) | 2.075 (2) | 2.0730 (14) | 2.0458 (15) |
| <i>M</i> (1)—N(1 <i>C</i>) | 2.152 (2) | | 2.0994 (15) | |
| <i>M</i> (1)—N(1 <i>D</i>) | 2.146 (2) | | 2.0988 (16) | |
| O(1 <i>L</i>)—N(1 <i>L</i>) | 1.310 (2) | 1.307 (2) | 1.3192 (19) | 1.3207 (19) |
| O(2 <i>L</i>)—N(2 <i>L</i>) | 1.292 (3) | 1.271 (3) | 1.295 (2) | 1.276 (2) |
| N(1 <i>L</i>)—N(2 <i>L</i>) | 1.288 (3) | 1.287 (3) | 1.288 (2) | 1.296 (2) |
| O(1 <i>L</i>)— <i>M</i> (1)—O(2 <i>L</i>) | 73.80 (7) | 75.63 (8) | 75.19 (5) | 77.19 (6) |
| O(2 <i>A</i>)— <i>M</i> (1)—O(2 <i>B</i>) | 89.96 (8) | | 88.17 (6) | |
| O(2 <i>B</i>)— <i>M</i> (1)—N(1 <i>D</i>) | 93.32 (9) | | 92.28 (6) | |
| O(2 <i>A</i>)— <i>M</i> (1)—N(1 <i>C</i>) | 89.46 (7) | | 90.17 (6) | |
| N(1 <i>C</i>)— <i>M</i> (1)—N(1 <i>D</i>) | 88.01 (8) | | 89.53 (6) | |
| O(1 <i>B</i>)— <i>M</i> (1)—N(1 <i>D</i>) | 96.21 (8) | | 93.57 (6) | |
| O(1 <i>A</i>)— <i>M</i> (1)—N(1 <i>C</i>) | 97.84 (8) | | 94.74 (6) | |
| O(1 <i>A</i>)— <i>M</i> (1)—O(1 <i>B</i>) | 157.94 (7) | | 159.00 (5) | |

structure. There is a positional disorder of the C1D atom (C1DX and C1DY) in the ethanol molecule; the C1D atom alternatively occupying one of the two positions. The sum of the site occupancy factors was constrained to be equal to 1.00 [0.738 (9) for C1DX]. The max/min ratio of the atom displacement parameters is somewhat large for the methyl C2D atoms of the ethanol molecule, which may be due to disorder.

The structures were solved by direct methods (*SHELXS97*) (Sheldrick, 1997*a*) and refined by full-matrix least-squares (*SHELXL97*) (Sheldrick, 1997*b*) on *F*² values. All non-H atoms were refined anisotropically. Hydrogen atomic positions were generated from assumed geometries, except for those of the O1D atom in (3). The ethanolic OH H atoms were located from a difference map. A riding model refinement was applied for the H atoms.

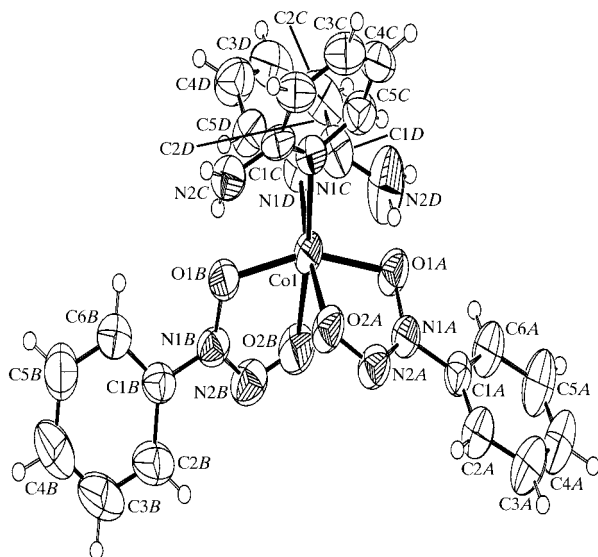


Figure 2

The molecular structure of (1) with displacement ellipsoids at the 50% probability level.

Table 3

Selected interatomic bond distances (Å) and bond angles (°) for (3).

| | (3 <i>a</i>) <i>X</i> = 1 | | (3 <i>b</i>) <i>X</i> = 2 | |
|---|----------------------------|---------------------|----------------------------|---------------------|
| | <i>L</i> = <i>A</i> | <i>L</i> = <i>B</i> | <i>L</i> = <i>C</i> | <i>L</i> = <i>D</i> |
| Co(<i>X</i>)—O(1 <i>L</i>) | 2.0479 (8) | | 2.0200 (9) | |
| Co(<i>X</i>)—O(2 <i>L</i>) | 2.0526 (8) | | 2.0801 (10) | |
| Co(<i>X</i>)—N(1 <i>L</i>) | | 2.2342 (8) | | |
| Co(<i>X</i>)—O(1 <i>L</i>) | | | | 2.1342 (11) |
| O(1 <i>L</i>)—N(1 <i>L</i>) | 1.3203 (11) | | 1.3235 (14) | |
| O(2 <i>L</i>)—N(2 <i>L</i>) | 1.2962 (13) | | 1.2827 (15) | |
| N(1 <i>L</i>)—N(2 <i>L</i>) | 1.2921 (12) | | 1.2949 (14) | |
| O(1 <i>L</i>)—Co(<i>X</i>)—O(2 <i>L</i>) | 77.01 (3) | | 76.62 (4) | |
| O(2 <i>L</i>)—Co(<i>X</i>)—O(1 <i>L</i>) ⁱ | 102.99 (3) | | 103.38 (4) | |
| N(1 <i>B</i>)—Co(<i>X</i>)—O(1 <i>A</i>) ⁱ | 90.82 (3) | | | |
| N(1 <i>B</i>)—Co(<i>X</i>)—O(2 <i>A</i>) ⁱ | 91.54 (3) | | | |
| O(1 <i>D</i>)—Co(<i>X</i>)—O(2 <i>C</i>) | | | 87.11 (5) | |
| O(1 <i>D</i>)—Co(<i>X</i>)—O(2 <i>C</i>) ⁱ | | | 92.89 (5) | |

Symmetry codes: for (3*a*) (i) $-x + 1, -y + 2, -z + 1$ and for (3*b*) (i) $-x + 1, -y + 1, -z + 2$.

Table 4

Selected interatomic distances (Å) and angles (°) for the hydrogen-bonding interaction in (1)–(3).

| Compound | <i>D</i> —H... <i>A</i> | H... <i>A</i> (Å) | <i>D</i> ... <i>A</i> (Å) | <i>D</i> —H... <i>A</i> (°) |
|----------|--|----------------------|------------------------------|--------------------------------|
| (1) | N(2 <i>C</i>)—H(21 <i>C</i>)...O(1 <i>B</i>) | 2.07 | 2.886 (3) | 159 |
| | N(1 <i>D</i>)—H(21 <i>D</i>)...O(1 <i>A</i>) | 1.98 | 2.812 (3) | 161 |
| | N(2 <i>C</i>)—H(22 <i>C</i>)...O(2 <i>A</i>) ⁱ | 2.17 | 2.984 (3) | 157 |
| | N(1 <i>D</i>)—H(22 <i>D</i>)...O(2 <i>B</i>) ⁱⁱ | 2.35 | 3.198 (3) | 171 |
| | N(2 <i>D</i>)—H(22 <i>D</i>)...N(2 <i>B</i>) ⁱⁱ | 2.21 | 2.990 (3) | 152 |
| (2) | N(2 <i>C</i>)—H(21 <i>C</i>)...O(1 <i>B</i>) | 2.04 | 2.858 (2) | 160 |
| | N(2 <i>D</i>)—H(21 <i>D</i>)...O(1 <i>A</i>) | 1.96 | 2.782 (3) | 161 |
| | N(2 <i>C</i>)—H(22 <i>C</i>)...O(2 <i>A</i>) ⁱ | 2.18 | 2.983 (2) | 156 |
| | N(2 <i>D</i>)—H(22 <i>D</i>)...O(2 <i>B</i>) ⁱⁱ | 2.43 | 3.274 (2) | 168 |
| | N(2 <i>D</i>)—H(22 <i>D</i>)...N(2 <i>B</i>) ⁱⁱ | 2.19 | 2.996 (2) | 157 |
| (3) | N(2 <i>B</i>)—H(21 <i>B</i>)...O(1 <i>A</i>) ⁱⁱⁱ | 2.38 | 3.137 (1) | 147 |
| | N(6 <i>B</i>)—H(61 <i>B</i>)...O(2 <i>A</i>) ⁱⁱⁱ | 2.05 | 2.855 (1) | 155 |
| | N(6 <i>B</i>)—H(62 <i>B</i>)...N(5 <i>B</i>) ^{iv} | 2.28 | 3.049 (1) | 149 |
| | N(2 <i>B</i>)—H(22 <i>B</i>)...O(1 <i>C</i>) | 2.16 | 2.992 (1) | 163 |
| | O(1 <i>D</i>)—H(1 <i>D</i>)...N(3 <i>B</i>) | 2.04 (3) | 2.862 (1) | 171 |

Symmetry codes: (i) $-x + 1, -y + 1, -z + 2$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x + 1, -y + 2, -z + 1$; (iv) $-x + 2, -y + 2, -z + 1$.

Tables 2 and 3 present selected molecular dimensions and Table 4 contains details of the hydrogen bonding. The (common) molecular structures of the $[M(\text{PhN}_2\text{O}_2)_2(2\text{-NH}_2\text{py})_2]$ complexes for *M* = Co and Ni (1 and 2, respectively) are shown in Fig. 2. Fig. 3 depicts the molecular structure of (3). Figs. 4 and 5 show aspects of the hydrogen-bonded hexagonal and pseudo-hexagonal grids. The molecular diagrams were prepared using *PLATON* (Spek, 1999) and the hydrogen-bonded schemes using *CERIUS*² (Molecular Simulations Inc., 1997).

3. Results and discussion

3.1. Crystal structures and molecular packing

3.1.1. $[\text{Co}(\text{PhN}_2\text{O}_2)_2(2\text{-NH}_2\text{py})_2]$ (1). The molecular structure of complex (1) consists of discrete monomeric units with the cobalt(II) atom in a distorted *cis*-octahedral configuration

defined by two chelating cupferronato anions (*A* and *B*) and two neutral 2-NH₂py ligands (*C* and *D*).

Intra- and intermolecular hydrogen-bond interactions are formed between the O and N atoms of the cupferronato anions and the H atoms of the NH₂ groups in complex (1). The short intramolecular N—H···O bonds (1.98 and 2.07 Å) formed with O(1*A*) and O(1*B*) atoms lying in apical positions, seem to stabilize the all-*cis* arrangement of the ligands. The rigidity of the planar CoN₂O₂ core with perpendicular Co—O bonds is advantageous to construct an infinite two-dimensional network maintained by intra- and intermolecular N—H···O and N—H···N hydrogen bonds. The N(2*C*) H atoms form one intra- and one intermolecular hydrogen bond directed to O(1*B*) and O(2*A*)ⁱ atoms, respectively. This chain is stretched between two centres of symmetry-equivalent Co atoms, which altogether results in a 12-membered ring within

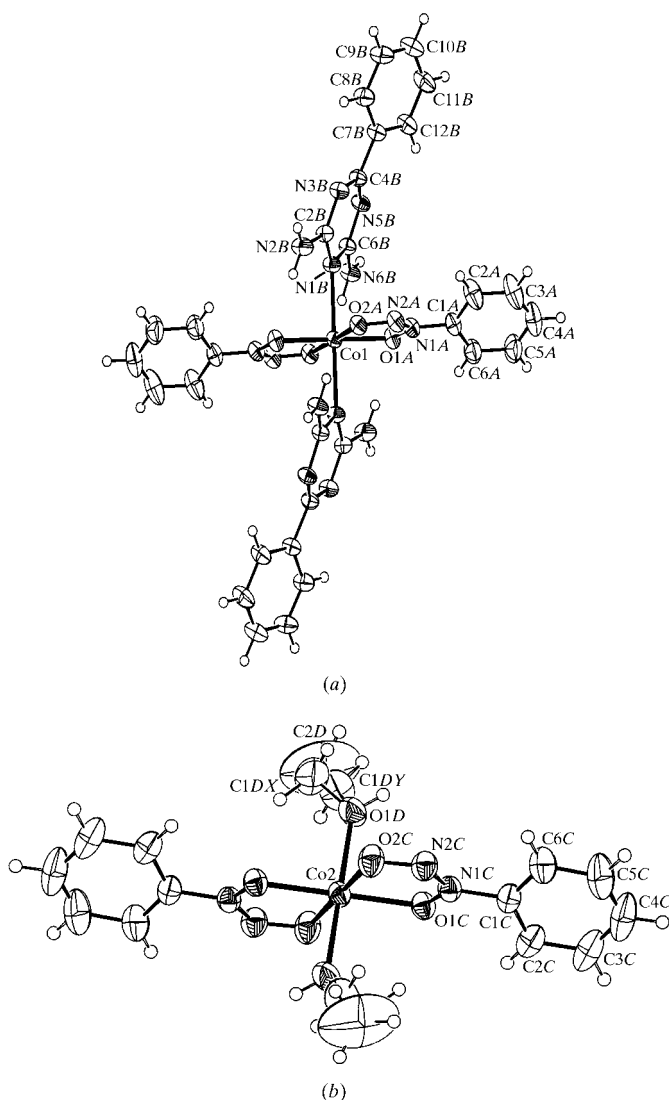


Figure 3
The molecular structure of (3); (a) and (b) show the two independent (3a) and (3b) molecules. Displacement ellipsoids are plotted at the 50% probability level. The ethanol ligand in (3b) has an orientational disorder and both two possible orientations are shown.

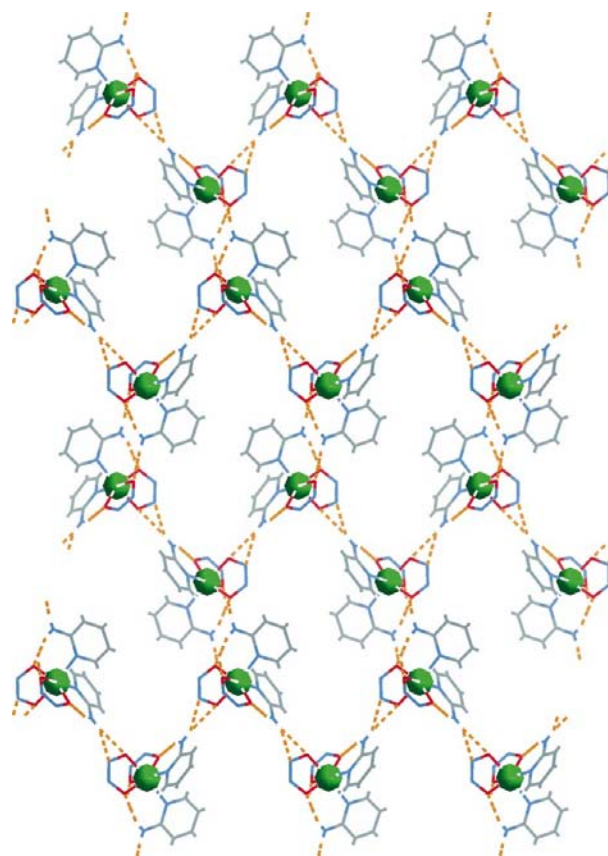


Figure 4
Section of the crystal structure of (1) showing the two-dimensional hexagonal grid formed through N—H···O/N hydrogen bonds. The Ph groups are omitted for clarity.

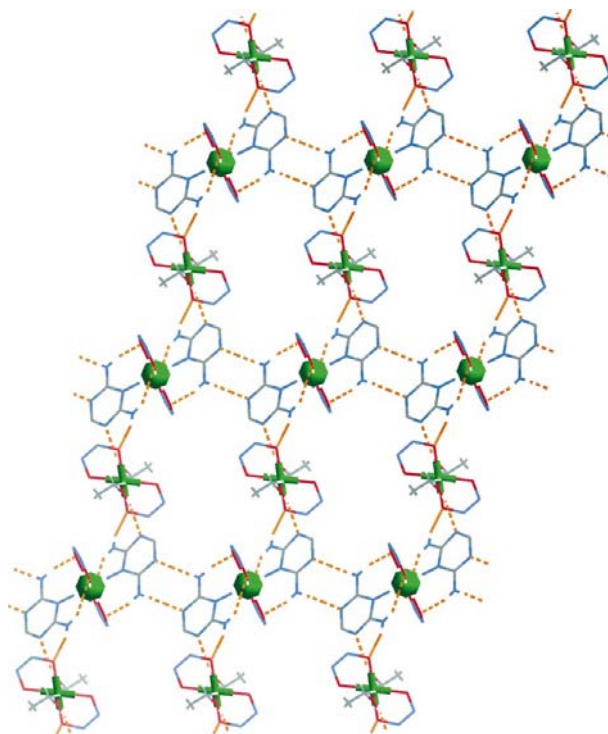


Figure 5
Section of the crystal structure of (3) showing the two-dimensional pseudohexagonal array, formed through N—H···O/N and O—H···N hydrogen bonds. The Ph groups are omitted for clarity.

the dimeric molecular aggregate. The remaining O(2*B*) and N(2*B*) atoms, protruding from the dimer, participate in bifurcated N—H···O and N—H···N hydrogen bonds. They link alternatively two full and two half dimers into a hexameric aggregate, which are connected by common edges generating a two-dimensional network {base vectors [0, 1, 0] and [1, 0, -1], plane (1, 0, 1)}, consisting of hexagonal grids. These hexagonal loops are occupied by the phenyl and pyridine moieties, which interact *via* π ··· π interactions (Dance & Scudder, 1995, and references therein; Janiak *et al.*, 1999, and references therein). The π ··· π stacking interactions are also present between the parallel hexagonal-grids sheets (Hardie *et al.*, 1999, and references therein).

The self-assembly of the two-dimensional hexagonal grid *via* hydrogen bonds is relatively frequent in organic supramolecular chemistry (Hardie *et al.*, 1999, and references therein), while it seems to be less common among the known structures in coordination chemistry (Subramanian & Zaworotko, 1994, and references therein). The best known examples of two-dimensional hexagonal grids formed through hydrogen bonding have been seen in various clathrates of urea (Hardie *et al.*, 1999, and references therein) and trimesic acid (Subramanian & Zaworotko, 1994, and references therein). Recently, Hardie *et al.* (1999, and references therein) reported that the 1,2-dicarbododecaborane(12) and cyclotrimeratrylene self-assemble through C/B—H···O hydrogen bonds into a two-dimensional hexagonal-grid network that incorporates bowl-shaped receptor sites. These built-in receptor sites bind 1,2-dicarbododecaborane(12) or fullerene C₇₀ molecules.

3.1.2. [Ni(PhN₂O₂)₂(2-NH₂py)₂] (2). Complex (2) is isostructural with the analogous cobalt(II) complex (1). The isostructurality index *I*(28) (for all non-H atoms) is 83% and the unit cell similarity index Π is 0.0044 (Kálmán & Párkányi, 1997). In a crystal lattice similar to (1) there is a supramolecular architecture built up by two-dimensional hexagonal grids of hydrogen-bonded molecules.

3.1.3. [Co(PhN₂O₂)₂(dpt)₂]·[Co(PhN₂O₂)₂(EtOH)₂] (3). The crystal lattice of (3) is built up from two different neutral cobalt(II) cupferronato complexes, [Co(PhN₂O₂)₂(dpt)₂] (3*a*) and [Co(PhN₂O₂)₂(EtOH)₂] (3*b*) in a 1:1 ratio. The formation of a crystal lattice from different neutral complexes is rather unusual and this is, to our knowledge, the first reported case for cobalt(II) complexes. Several crystal lattices are known, however, built up from different anionic and cationic cobalt(II) complexes (Cotton *et al.*, 1998, and references therein).

In (3) both (3*a*) and (3*b*) subunits contain the cobalt(II) atom sitting in the centre of symmetry in an almost ideal *trans*-octahedral configuration. The two chelating cupferronato anions are in the equatorial plane while the two neutral donor molecules, dpt in (3*a*) and EtOH in (3*b*), are placed in perfect axial positions. In (3*a*) the dpt molecule is coordinated to the Co(1) atom *via* its N(1) atom. Coordination *via* either N(3) or N(5) atoms is sterically hindered by the 4-phenyl ring protruding from the molecule. Moreover, only this coordination provides favourable positions to the NH₂ groups to donate hydrogen bonds to the cupferronato oxygen atoms.

The Co(1)—N(1*B*) bond length of 2.2354 (9) Å is almost equal to that of 2.23 Å reported for the B₁₂ coenzyme (Lenhert, 1968). In (3*a*) all O atoms of the cupferronato ligand act as acceptors of intramolecular N—H···O hydrogen bonds. The intramolecular hydrogen bonds in (3*a*) generate four six-membered rings. An infinite row of molecules of (3*a*) is self-assembled by intermolecular N—H···N hydrogen bonds of 2.28 Å. These interactions build up eight-membered rings between every two complementary dpt units, leading to infinite chains. Moreover, each molecule of (3*a*) is crosslinked to the neighbouring (3*b*) molecules by N—H···O and O—H···N hydrogen bonds. The remaining H atoms of the NH₂ groups of (3*a*) are linked to the O atoms of the (3*b*) cupferronato ligands. The OH H atoms of the ethanol ligand saturate the remaining hydrogen-bonding sites of (3*a*) by interacting at each free triazinic N(3) position through an O—H···N link. These concurrent N—H···O and O—H···N interactions also form eight-membered rings between the neighbouring (3*a*) and (3*b*) subunits and establish the infinite linear chains of (3*a*). The self-assembly of (3*a*) and (3*b*) subunits, therefore, generates intercalate bridges across the infinite linear chains. These (3*a*) chains are crosslinked by (3*b*) ‘spacers’, forming a novel chain of {*ab*}_{*n*}-type. The two chains create an angle of *ca* 75°. Two parallel {*ab*}_{*n*} chains using six cobalt centres close a loop occupied by the phenyl rings, which are held together by π ··· π interactions (Dance & Scudder, 1995, and references therein; Janiak *et al.*, 1999, and references therein). The two-dimensional network {base vectors [1, 0, 0] and [0, 1, -1], plane (0, 1, 1)}, maintained by the hydrogen bonds presents pseudohexagonal grid motifs. The neighbouring sheets are related by π ··· π interactions and these interactions influence the nature of hydrogen bonding and *vice versa* (Sharma *et al.*, 1993, Janiak *et al.*, 1999, and references therein).

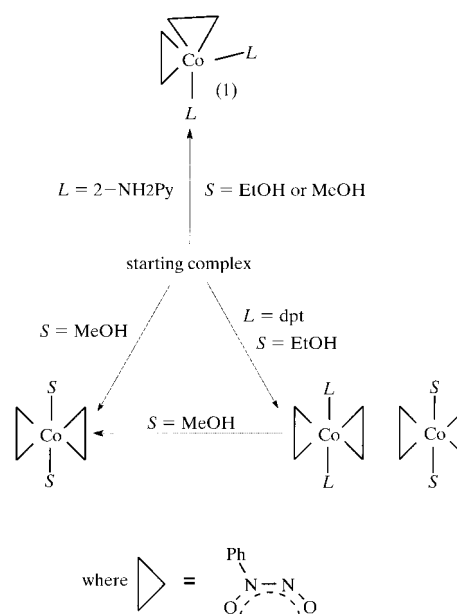


Figure 6

The hexacoordinate cobalt(II) cupferronato adducts showing the additional neutral *N*-donor ligands and the competition between solvent molecules.

3.2. Influence of the solvent molecules on hydrogen-bond formation

In (1) and (2) the number and orientation of hydrogen-bond donor and acceptor sites are adequate to a self-assembly of two-dimensional hexagonal-grid type network and do not require the assistance of solvent molecules. This is supported by the fact that crystallization from EtOH or MeOH yields isostructural crystals of (1) and (2). In contrast, the crystal lattice of (3) could only be obtained from ethanol (Fig. 6). When methanol was used, the crystals turned into the $[\text{Co}(\text{PhN}_2\text{O}_2)_2(\text{MeOH})_2]$ complex (Deák *et al.*, 1998). Interestingly, in (3) ethanol has a special cooperative effect by forming (3*b*). In other words, the solvent molecule in (3*b*) coordinates to the cobalt(II) centres and participates in both coordinate and hydrogen-bond interactions. The solvent role in this system is more complex than a templating or space-filling function played generally in other hydrogen-bonded networks (Desiraju, 1991; Hardie *et al.*, 1999, and references therein; Janiak *et al.*, 2000). The (3*b*) subunit with its ethanol and cupferronato functions provides:

(i) the maximal number of hydrogen bonds within the complementary functions of (3*a*) and (3*b*);

(ii) a structural integrity of the hydrogen-bonded arrays;

(iii) the self-assembly of the two-dimensional network.

Crystallization of (3) from ethanol *versus* the lattice spoiling effect of methanol resulting in the exclusive formation of $[\text{Co}(\text{PhN}_2\text{O}_2)_2(\text{MeOH})_2]$ (Deák *et al.*, 1998) reveals a solvent competition, *i.e.* in these complexes the solvent dictates which hydrogen bond array is formed. The competition between the coordination capacity of the alcohol and *N*-donor molecules may also in part influence which of the cobalt(II) cupferronato adducts is formed.

4. Conclusions

We reported on the possibilities of creating infinite hydrogen-bonded two-dimensional frameworks based on coordination complexes in which the complementary functions of the different multifunctional hydrogen-bond acceptor and donor ligands govern the self-assembly *via* hydrogen bonds and $\pi \cdots \pi$ stacking interactions. The self-assembly of cobalt(II) and nickel(II) octahedra formed by cupferronato and neutral *N*-donor ligands and their NH_2 functions leads to extended two-dimensional hexagonal and pseudo-hexagonal grid-type networks. We gave evidence that the solvent molecules also play an important role in such systems.

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