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Facile synthesis of heterotrimetallic metal-string complex [NiCoRh(dpa)₄Cl₂] through direct metal replacement

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Experimental Section

Physical measurements

The crystals were mounted on a glass fiber. Crystal data were collected on a NONIUS Kappa CCD diffractometer with monochromatized Mo-Ka radiation (*lambda* = 0.71073 Å) at T = 150(2) K for **1**, **2**, **3** and **4**. Cell parameters were retrieved and refined using *DENZOSMN* software on all observed reflections. Data reduction was performed with the *DENZO-SMN* software. An empirical absorption was based on the symmetry- equivalent reflections and absorption corrections were applied with the SORTAV program. All the structures were solved by using the *SHELXS-97* and refined with *SHELXL-97* by full-matrix least squares on F^2 values. The hydrogen atoms were included in calculated positions and refined with a riding model. IR spectra were obtained with a Nicolet Fourier-Transform in the range 400–4000 cm⁻¹. FAB mass spectra were obtained with a JEOL HX-110 HF double-focusing spectrometer operating in the positive ion detection mode. ¹H NMR spectra were recorded with a Bruker AMX 300 MHz spectrometer. Magnetic measurements were carried out with a Quantum Design MPMS7 SQUID magnetometer operating at a magnetic field of 3000 G between 4 and 300 K. The diamagnetic corrections were evaluated from Pascal's constants.

Synthesis

[CoCoRh(dpa)₄Cl₂] (1):

The RhCl₃·XH₂O (127 mg, 0.5 mmol) was dissolved in 5 mL MeOH in a 250-mL Erlenmeyer flask to which 35 g naphthalene was added with complete mixing. After that, the MeOH was dried by vacuum. Hdpa (342 mg, 2 mmol) and CoCl₂ (128 mg, 1mmol) were mixed with the previous mixture and it was heated at 180°C for 1 hours first and at 220°C for 2 hours under Argon. The solution turned to blue gradually. A solution of *t*-BuOK (224 mg, 2 mmol) in n-butanol (7 mL) was added dropwise. The resulting dark green mixture was continually refluxed for another half hour. The mixture was then cooled to 80°C, and treated with hexane (300 mL) to precipitate the metal complex. The solid was washed with hexane to remove naphthalene and was subsequently extracted with 100 ml CH₂Cl₂. The dark green crystal was obtained by layering of ether with the CH₂Cl₂ solution of complex. (119 mg, 49% yield). IR (KBr, cm⁻¹): 1606 m, 1593 m, 1546 m, 1469 s, 1427 s, 1359 s, 1316 m, 1152 m, 1028 m, 881 m, 759 m, 735 m. MS(FAB) *m/z*: 971 [M]⁺, 936 [M-Cl]⁺, 901[M-2Cl]⁺; ¹H NMR (300 MHz, CD₂Cl₂): δ (ppm) 133.17 (b, 1H), 73.18 (1H), 51.77 (1H), 25.31

(1H) , 12.26 (1H), 9.39 (1H), -4.27 (1H) , -4.94 (1H). Elemental analysis (%) [CoCoRh(dpa)₄Cl₂]: calcd. C 49.43, H 3.21, N 17.30; found: C 49.46, H 3.35, N 17.19

[NiCoRh(dpa)₄Cl₂] (2):

In a 50 mL Erlenmeyer flask, $[CoCoRh(dpa)_4Cl_2]$ (1) (100 mg, 0.1 mmol) and Ni(OAc)₂·4H₂O (35 mg, 0.14 mmol) were refluxed in naphthalene (14 g) under Argon and kept at this temperature for 1 hour. After cooling to ca. 80° C, the solution was poured into hexane (100 mL) and then filtered. The crude material was washed with hexane (50 mL) to remove naphthalene. CH₂Cl₂ (40 mL) was added to extract the product. The solution was then condensed to 20 mL. The dark green crystal was formed by layering the CH₂Cl₂ solution with ether. Yield: 89 mg, 89 %. IR (KBr, cm⁻¹): 1608 m, 1595 m, 1545 m, 1459 s, 1432 s, 1365 s, 1319 m, 1167 m, 1153 m, 1028 m, 881m, 758 m, 735 m. MS(FAB) *m*/*z*: 935 [M-Cl]⁺; ¹ H NMR (300 MHz, CD₂Cl₂): δ (ppm) 16.92 (b, 1H), 10.76 (b, 1H), 9.72 (d, 1H), 8.03 (d, 1H) , 7.53 (t, 1H), 7.21 (t, 1H), 6.19 (d, 1H) , 6.05 (t, 1H). Elemental analysis (%) [NiCoRh(dpa)_4Cl_2]: calcd. C 49.48, H 3.22, N 17.32; found: C 49.52, H 3.31, N 17.28

[NiCoRh(dpa)₄Cl](PF₆) (3):

The [NiCoRh(dpa)₄Cl₂] (2) (89 mg 0.082 mmol) in 30 mL CH₂Cl₂ was treated with TlPF₆ (29 mg, 0.082 mmol). The mixture was stirred for 2 days and the solid was collected by filtration. The solid was dissolved in 20 mL of acetone and then filtered again to remove TlCl. The crystals were collected after layering with ether. Single crystals suitable for X-ray diffraction studies were obtained by slow diffusion of Et₂O into Acetone/CH₂Cl₂(1:1) solution of complex. Yield: 73 mg, 74 %. IR (KBr, cm⁻¹): 1609 m, 1597 m, 1546 w, 1467 s, 1432 s, 1381 m, 1365 m, 1159 m, 1029 m, 853 s, 761 m, 737w. MS(FAB) *m/z*: 935 [M]⁺; ¹ H NMR (300 MHz, Acetone-d₆): δ (ppm) 9.92 (d, 1H), 8.96 (d, 1H), 7.27-7.18 (m, 2H), 6.77-6.70 (m, 2H) , 6.56 (d, 1H), 6.42 (d, 1H). Elemental analysis (%) [NiCoRh(dpa)₄Cl](PF₆): calcd. C 44.44, H 2.99, N 15.56; found: C 44.49, H 3.10, N 15.51

[NiCoRh(dpa)₄Cl₂](PF₆) (4):

The [NiCoRh(dpa)₄Cl₂] (2) (85 mg 0.088 mmol) was dissolved in 30 mL CH₂Cl₂ and then FcPF₆(45 mg, 0.13 mmol) was added into the green solution. A dark blue solution was formed instantly. After 10 minutes, the mixture was filtered and the dark blue crystals were obtained by layering the blue solution with ether. IR (KBr, cm⁻¹): 1601 m, 1549 m, 1546 m, 1467 s, 1428 s, 1363 m, 1310 m, 1223 m,1159m, 1029 m, 841s, 767m, 740m. MS(FAB) m/z (%): 971 [M]⁺, 936 [M-Cl]⁺, 901[M-2Cl]⁺; ¹H NMR (300 MHz, CDCl₃): δ (ppm) 25.25 (b, 1H), 24.10 (b, 1H), 22.86 (b, 1H), 15.32 (b, 1H) , 11.00 (b, 1H), -13.55 (b, 1H), -23.42 (b, 1H) , -29.13 (b, 1H). Elemental analysis (%) NiCoRh(dpa)₄Cl₂](PF₆): calcd. C 43.05, H 2.89, N 15.07; found: C 43.13, H 3.06, N 15.02



Figure. S1 ORTEP view of the molecular structure [CoCoRh(dpa)₄Cl₂] (1) (50% probability). Hydrogen atoms and interstitial solvents have been omitted for clarity. Selected bond distances (Å) (averaged) are as follows: Disordered occupancy 50/50%, Co2–M1 2.3362 (4), Co2-M2 2.3566 (4), Co2–N 1.922 (2), M1–Cl1 2.4845 (7), M2–Cl2 2.5173 (7), M1–N 2.018 (2), M2–N 2.046 (2). M1 and M2 represent the mixture of Co and Rh atoms according to the ratio of disordered occupancy. Crystal data: C₄₄H₄₂Cl₂N₁₂Co₂Rh₁, *M*w = 1046.57, monoclinic, space group *P*2₁/*c*, *a* = 15.9265(3) Å, *b* = 15.7081(3) Å, *c* =16.9952(3) Å, α = 90°, β = 98.7514(11)°, γ = 90°, *V* = 4202.27(13) Å³, *Z* = 4, *d* (calcd.) = 1.654 Mg/m³, T = 150(2) K, 25058 reflection collected, 9595 independent, *R*_{int}= 0.0373, *R*₁ = 0.0669, w*R*₂ = 0.0883 for all data.



Figure S2: ¹H NMR spectrum of [CoCoRh(dpa)₄Cl₂] (1) in CD₂Cl₂





The paramagnetic signal at 16.92 ppm was undetectable in 2D COSY due to its fast relaxation time and this broad signal was contributed by paramagnetic center of Ni atom. On the contrary, the protons of pyridyl ring coordinated to diamagnetic $(CoRh)^{4+}$ center were determined by the 2D COSY spectrum. According to the coupling constant of pyridyl ring, the value in meta position is higher than ortho position. Therefore, the doublet peaks of H₁ and H₄ could be distinguished as shown in figure.



Figure S4: High resolution FAB spectrum (black) and its simulation (red) of [NiCoRh(dpa)₄Cl₂] (2)



Figure S5: ¹H NMR spectrum of [NiCoRh(dpa)₄Cl](PF₆) (3) in Acetone-d₆.
Comparing the ¹H NMR spectrums between [NiCoRh(dpa)₄Cl₂] (2) and [NiCoRh(dpa)₄Cl](PF₆)
(3), The chemical shift of H₁ is only slightly changed from 9.72 to 9.92 ppm. This proton was assigned in the pyridyl ring which was bound to the Rh atom, because the chemical structure of diamagnetic center (CoRh)⁴⁺ was identical between compound 2 and 3. Subsequently, the other pyridyl protons could be determined by its 2D COSY spectrum (Figure 2 in article).



Figure S6: Temperature dependence of the magnetic moment μ_{eff} for [NiCoRh(dpa)₄Cl₂] (2) and [NiCoRh(dpa)₄Cl](PF₆) (3).