Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Two-Dimensional Frameworks Formed by Pentagonal Bipyramidal Cobalt(II) Ion and Hexacyanometallates: Antiferromagnetic Ordering, Metamagnetism and Slow Magnetic Relaxation

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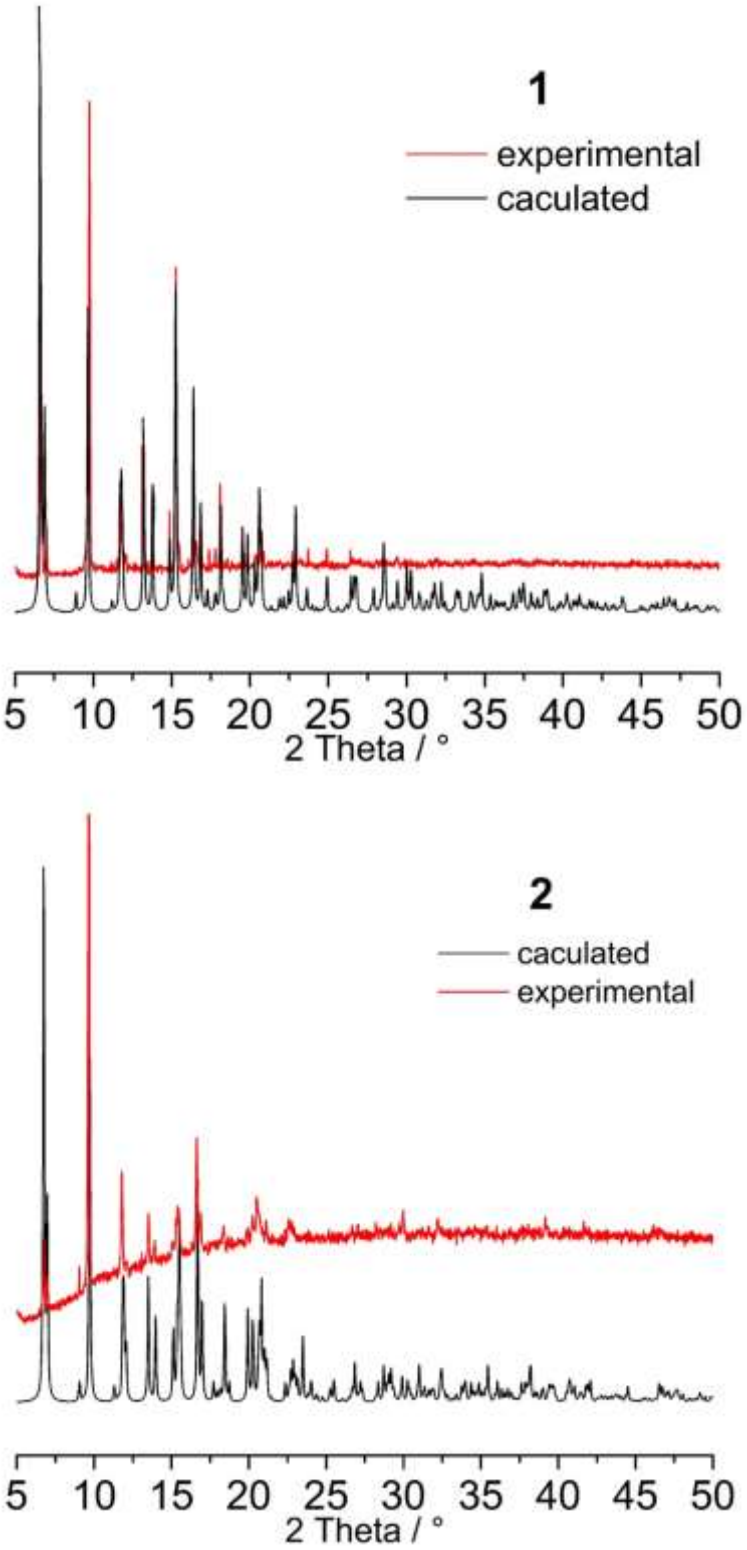

Figure S1. The PXRD of **1** and **2**.

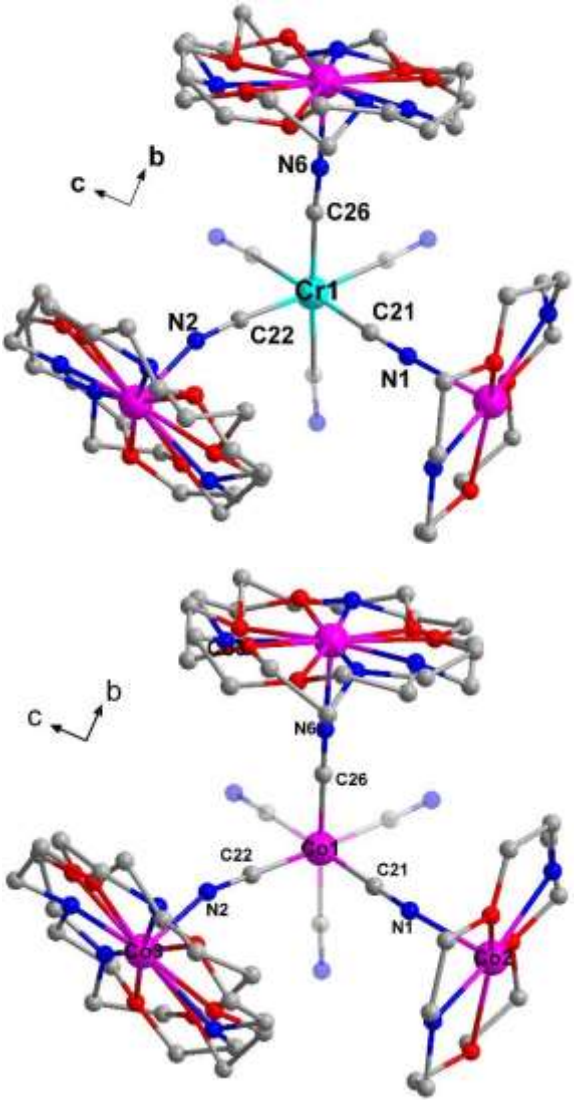

Figure S2. The Co_3M units of **1** and **2** bridged by the cyanides in the facial positions

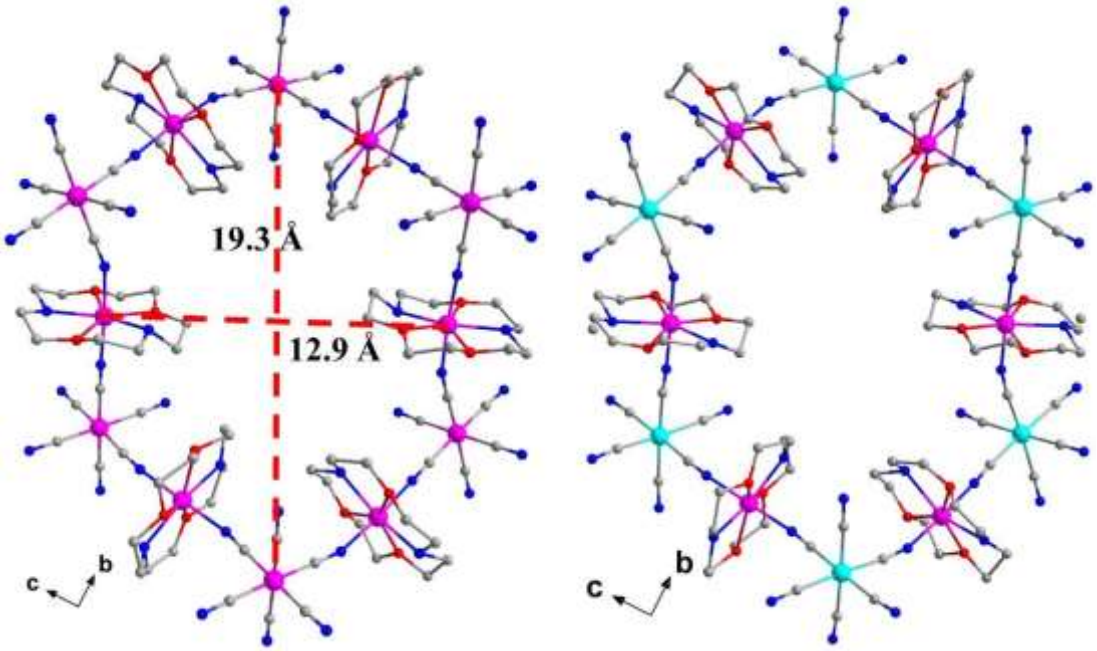

Figure S3. Hexagonal twelve-metallic rings of **1** and **2**.

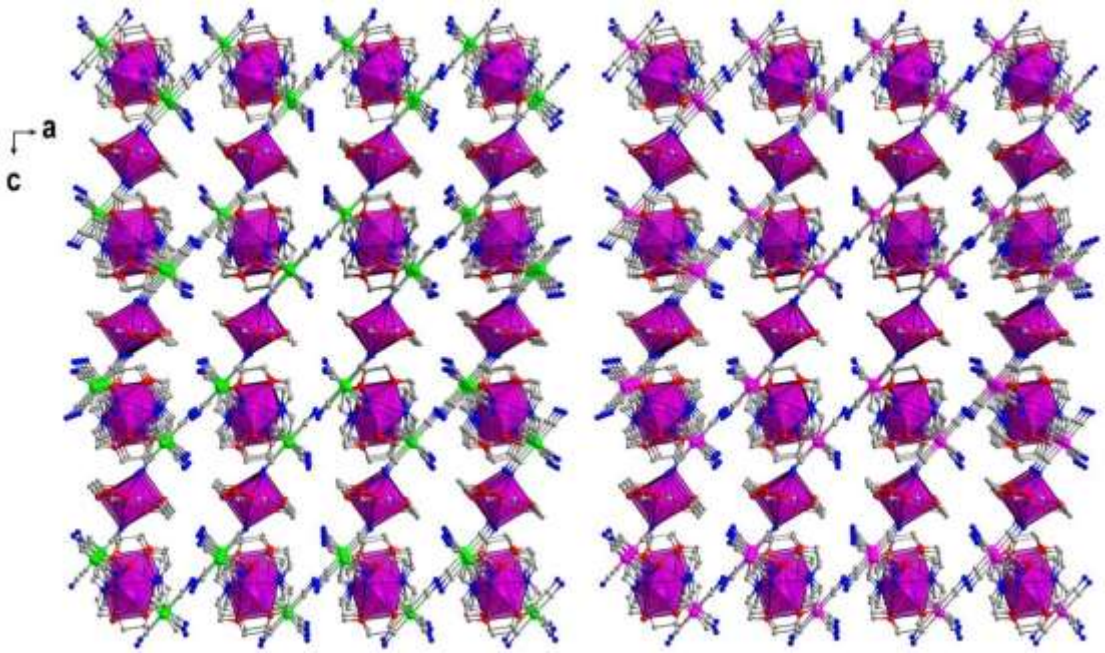

Figure S4. The packing structures of **1** and **2** along the *b* direction.

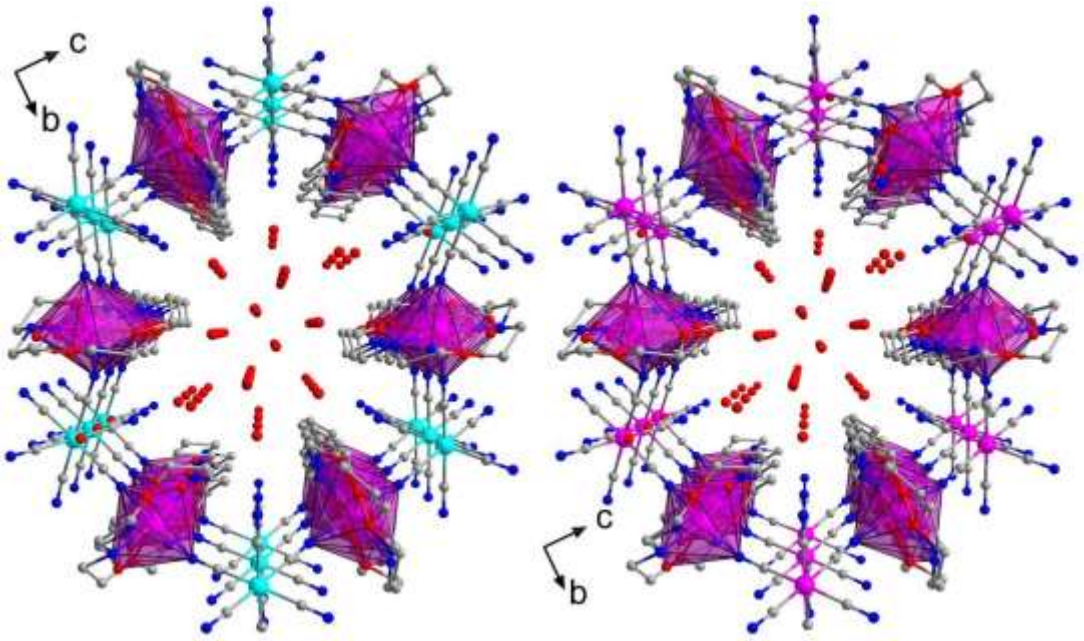

Figure S5. The water molecules locate in the 1D pores of **1** and **2**.

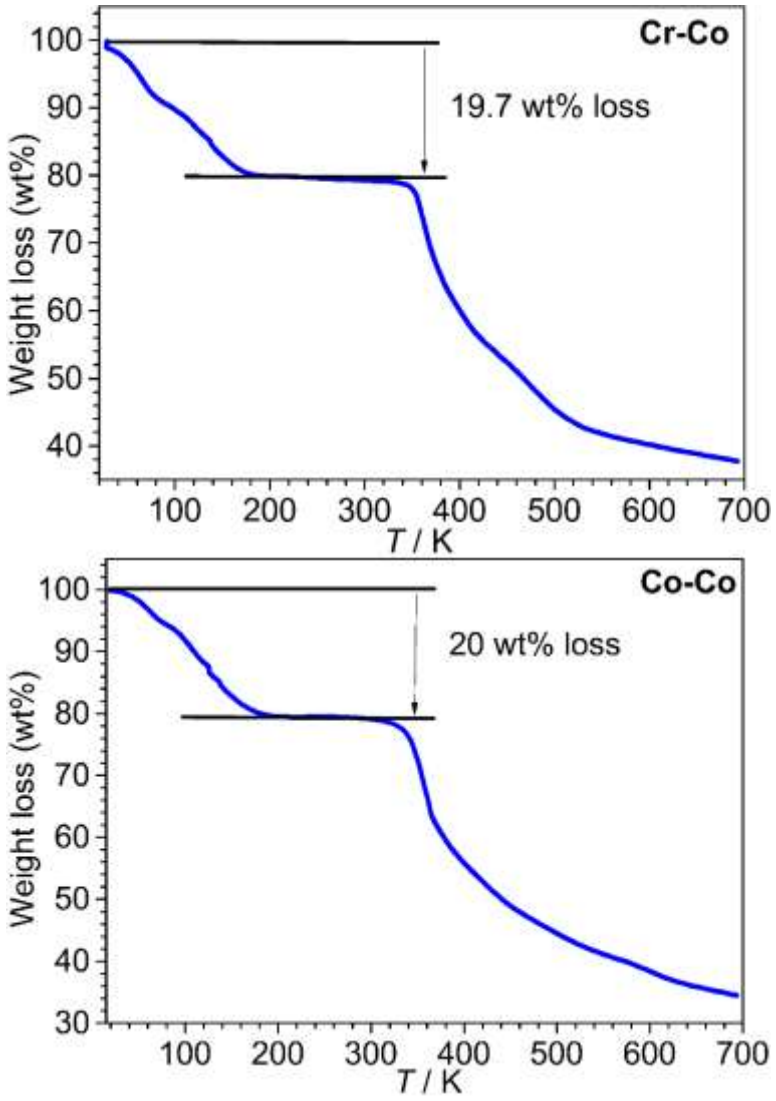

Figure S6. The thermal gravimetric analysis (TGA) data of **1** and **2**.

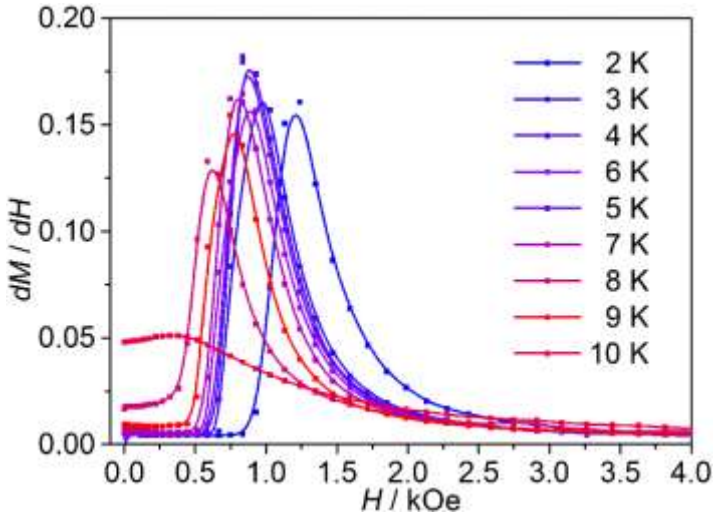

Figure S7. The differentials of the magnetization (d*M /dH vs H)* of **1**.

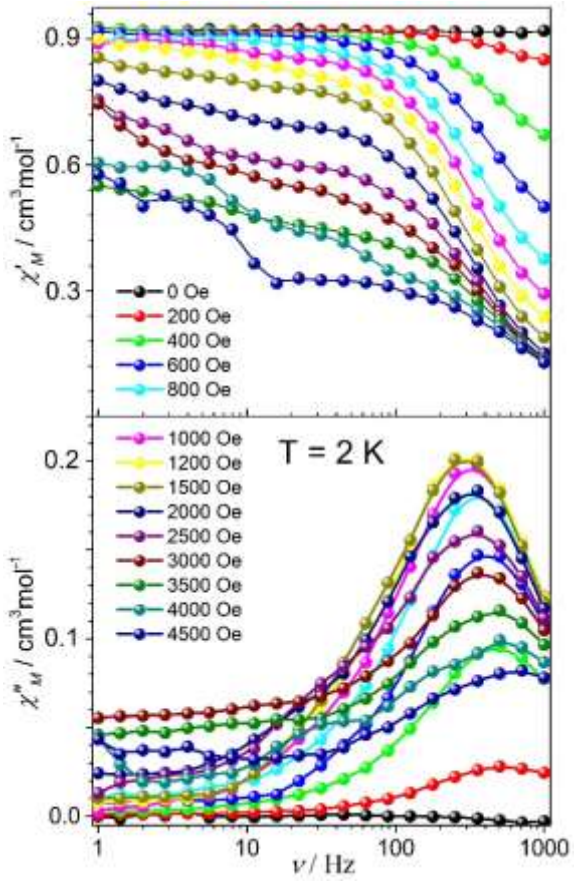

Figure S8. Frequency dependence of the in-phase (χ′) and out-of-phase (χ″) magnetic susceptibility of **2** (1–1000 Hz) measured at 2 K in various applied fields from 0 to 4500 Oe.

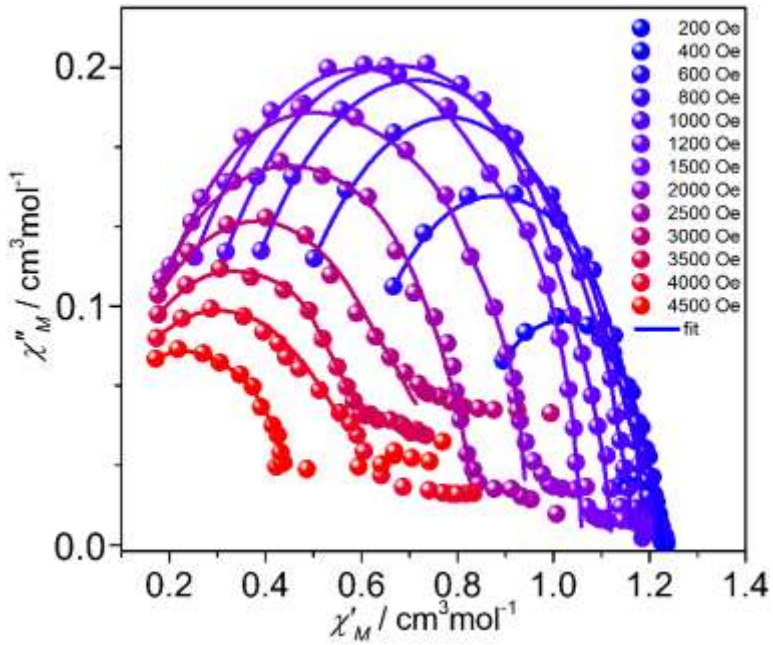

Figure S9. Cole–Cole plots of χ' vs. χ'' of **2** at 2 K under various applied dc fields. The solid lines represent the best fit of the experimental results with the generalized Debye model.

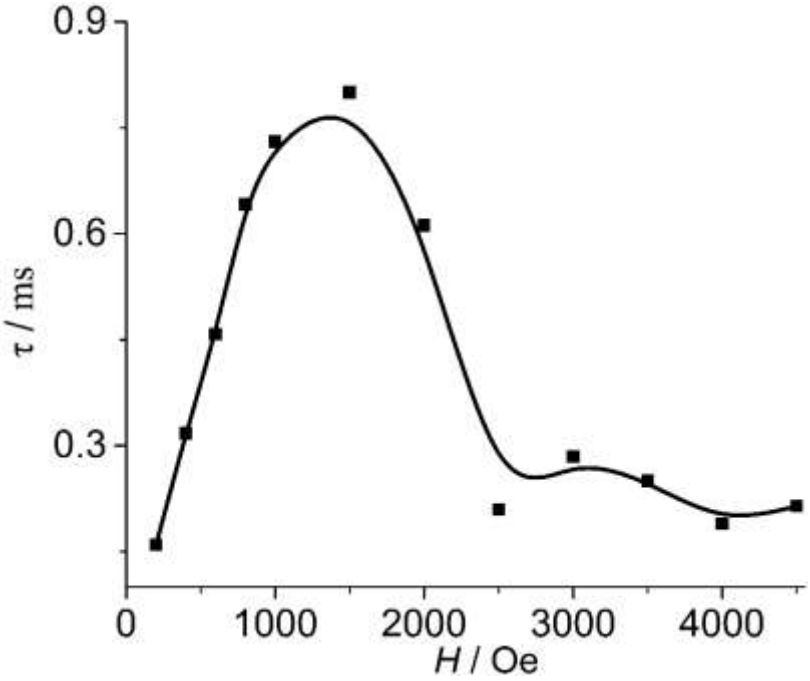

Figure S10. Field dependence of the magnetic relaxation time at 2 K for **2**.

Table S1. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1					
Co1-N1	2.098(5)	**Co1-N5**	2.112(5)	**Co1-N8**	2.211(4)
Co1-N2	2.255(5)	**Co1-N7**	2.260(5)	**Co1-N9**	2.274(4)
Co1-N4	2.115(5)				
N8-Co1-N9	174.71(16)	N4-Co1-N8	96.73(17)	N4-Co1-N9	88.40(17)
N2-Co1-N7	88.32(16)	N5-Co1-N8	94.72(17)	N5-Co1-N9	87.77(17)
2					
Co1-N1	2.091(3)	**Co1-N4**	2.343(3)	**Co1-N2#1**	2.263(2)
Co1-N2	2.263(2)	**Co1-N5**	2.208(3)	**Co1-N3#1**	2.119(2)
Co1-N3	2.115(5)				
N5-Co1-N4	178.60(12)	N5-Co1-N2#1	92.90(7)	N5-Co1-N2	92.90(7)
N3#1-Co1-N2	145.06(10)	N1-Co1-N4	87.38(12)	N3-Co1-N4	93.19(9)
#1 x,-y+1/2,z; #2 x+1/2,y,-z+3/2; #3 x+1/2,-y+1/2,-z+3/2; #4 x-1/2,y,-z+3/2					

Table S2. Relaxation fitting parameters from the least-square fitting of the Cole-Cole plots of **2** according to the generalized Debye model.

T / K	χ_S / $cm^3mol^{-1}K$	χ_T / $cm^3mol^{-1}K$	τ / s	α
1.8	0.22919	1.12823	9E-4	0.15397
1.9	0.26684	1.08999	8.5E-4	0.13309
2.0	0.25931	1.05751	8E-4	0.16988
2.1	0.2933	1.01486	6.4E-4	0.16875
2.2	0.2805	1.01176	5.2E-4	0.20581
2.3	0.2705	1.01695	4.3E-4	0.26735
2.4	0.30528	0.96329	3.5E-4	0.2388
2.5	0.31289	0.95101	2.8E-4	0.2123
2.6	0.31066	0.94745	2.3E-4	0.29686
2.7	0.31896	0.93998	2E-4	0.29736
2.8	0.33381	0.90457	1.7E-4	0.3
2.9	0.35059	0.8673	1.5E-4	0.33993
3.0	0.38322	0.83027	1.3E-4	0.3

Explanation of Checkcif Alerts

Datablock: CrCo

Alert level A

PLAT415_ALERT_2_A Short Inter D-H..H-X	H15G .. H19C .. 1.33 Ang.
PLAT417_ALERT_2_A Short Inter D-H..H-D	H9 .. H14H .. 1.46 Ang.
PLAT417_ALERT_2_A Short Inter D-H..H-D	H7E .. H12G .. 0.88 Ang.
PLAT417_ALERT_2_A Short Inter D-H..H-D	H12H .. H14G .. 1.66 Ang.

Alert level B

PLAT415_ALERT_2_B Short Inter D-H..H-X	H14G .. H17D .. 1.90 Ang.
PLAT415_ALERT_2_B Short Inter D-H..H-X	H14H .. H17D .. 1.95 Ang.
PLAT417_ALERT_2_B Short Inter D-H..H-D	H7E .. H12H .. 2.05 Ang.
PLAT417_ALERT_2_B Short Inter D-H..H-D	H8E .. H11G .. 1.98 Ang.
PLAT417_ALERT_2_B Short Inter D-H..H-D	H8F .. H9F .. 1.95 Ang.
PLAT417_ALERT_2_B Short Inter D-H..H-D	H9F .. H11H .. 1.94 Ang.
PLAT417_ALERT_2_B Short Inter D-H..H-D	H10F .. H13G .. 1.92 Ang.
PLAT417_ALERT_2_B Short Inter D-H..H-D	H11G .. H13G .. 1.95 Ang.
PLAT417_ALERT_2_B Short Inter D-H..H-D	H11H .. H13G .. 2.01 Ang.
PLAT417_ALERT_2_B Short Inter D-H..H-D	H15G .. H9' .. 1.81 Ang.
PLAT420_ALERT_2_B D-H Without Acceptor	O11 -- H11H ... Please Check

Author Response: These alerts are all related to the hydrogen atoms of lattice water molecules. It is very difficult to locate hydrogen atoms accurately using X-ray data because these atoms have low scattering power. In addition, the severe disorder in the complex makes the situation even worse. We have used two methods to add the hydrogen atoms of the water molecules, including DIF-Fourier maps and HADD instructions. The current results using HADD instructions are the best.

PLAT242_ALERT_2_B Low 'MainMol' Ueq as Compared to Neighbors of Co2 Check

Author Response: The U(eq) value of an atom is compared with the average U(eq) for to non-hydrogen atoms bonded to it. Large differences may indicate that the wrong atom type was assigned. Since the compound 1 is isostructural to 2, the atom type of Co2 is undoubtedly correct in our case. The severe disorder of our structure and the low site occupancy of the coordination atoms might cause their low U_{eq} compared to the metal ion Co2.

Datablock: CoCo

Alert level A

PLAT415_ALERT_2_A Short Inter D-H..H-X	H13B .. H15H .. 1.50 Ang.
PLAT415_ALERT_2_A Short Inter D-H..H-X	H14G .. H17C .. 1.28 Ang.
PLAT415_ALERT_2_A Short Inter D-H..H-X	H15G .. H20C .. 1.84 Ang.
PLAT417_ALERT_2_A Short Inter D-H..H-D	H9 .. H14G .. 1.76 Ang.
PLAT417_ALERT_2_A Short Inter D-H..H-D	H8E .. H11G .. 1.16 Ang.
PLAT417_ALERT_2_A Short Inter D-H..H-D	H8F .. H9F .. 1.63 Ang.
PLAT417_ALERT_2_A Short Inter D-H..H-D	H12H .. H14G .. 1.62 Ang.
PLAT417_ALERT_2_A Short Inter D-H..H-D	H13H .. H14H .. 1.76 Ang.

Alert level B

PLAT415_ALERT_2_B Short Inter D-H..H-X H8F H16A .. 2.08 Ang.
PLAT415_ALERT_2_B Short Inter D-H..H-X H11 H .. H14C .. 2.06 Ang.
PLAT415_ALERT_2_B Short Inter D-H..H-X H14 H .. H17C .. 2.01 Ang.
PLAT417_ALERT_2_B Short Inter D-H..H-D H9 H14H .. 1.93 Ang.
PLAT417_ALERT_2_B Short Inter D-H..H-D H7F H8E .. 2.03 Ang.
PLAT417_ALERT_2_B Short Inter D-H..H-D H7F H8F .. 1.92 Ang.
PLAT417_ALERT_2_B Short Inter D-H..H-D H15G H9' .. 1.86 Ang.
PLAT420_ALERT_2_B D-H Without Acceptor O11 H11H ... Please Check

Author Response: These alerts are all related to the hydrogen atoms of lattice water molecules. It is very difficult to locate hydrogen atoms accurately using X-ray data because these atoms have low scattering power. In addition, the severe disorder in the complex makes the situation even worse. We have used two methods to add the hydrogen atoms of the water molecules, including DIF-Fourier maps and HADD instructions. The current results using HADD instructions are the best.