Supporting Information

3d-4f Heterometallic Complexes through the Reduction of Transition Metal Carbonyls by Bulky Ln^{II} Amidinates

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1. IR Spectra

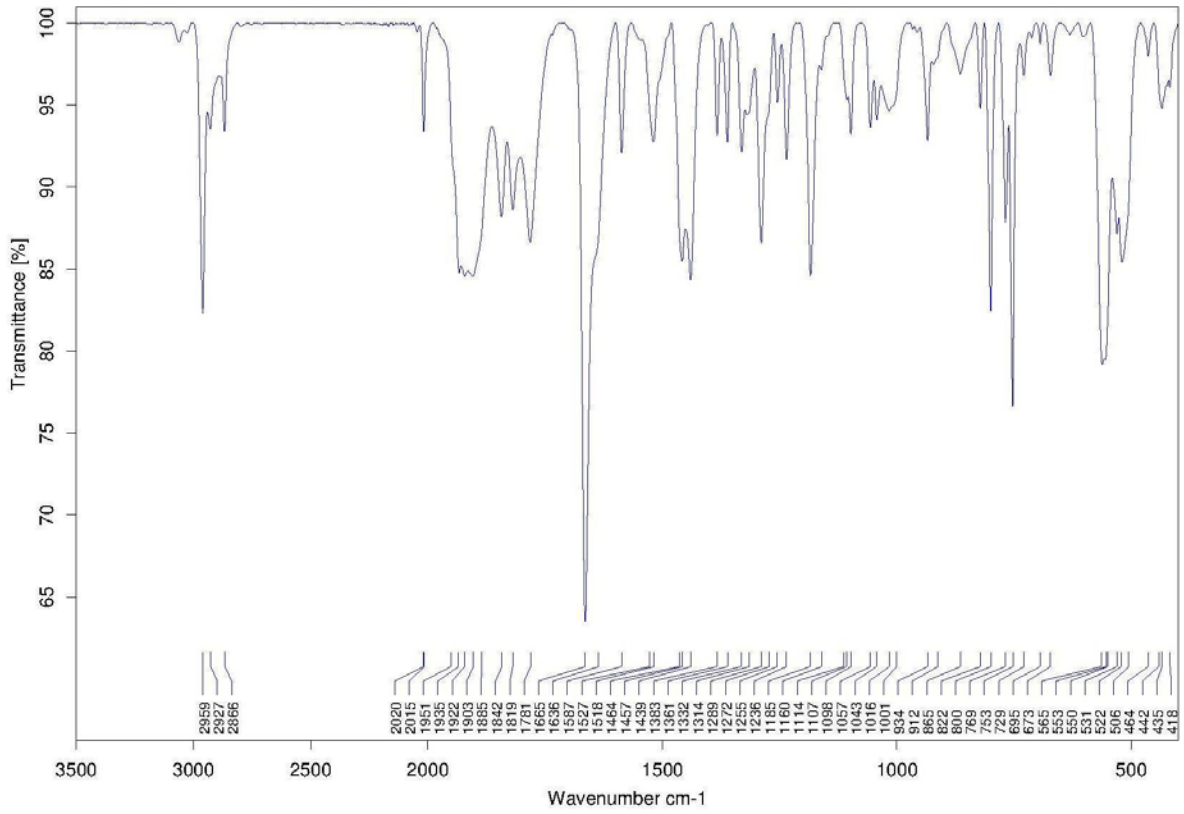

Figure S1: IR spectrum of complex **1**.

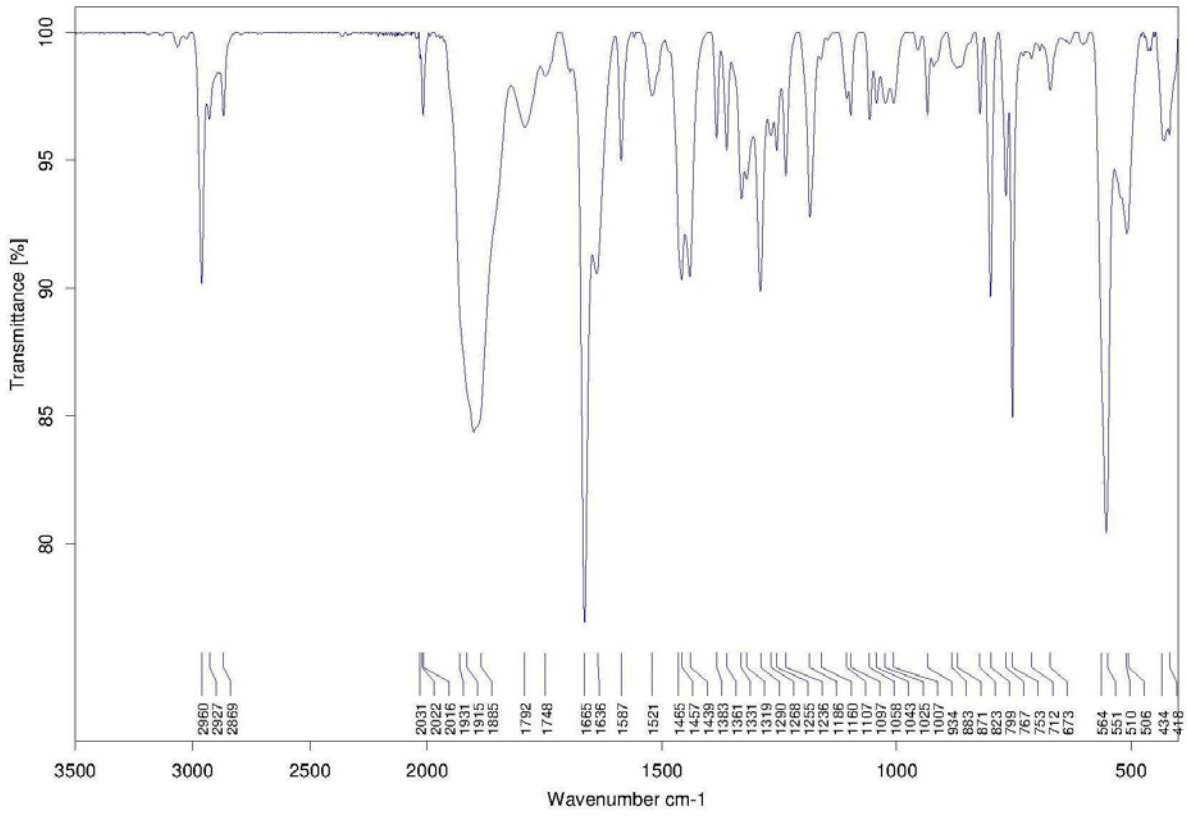

Figure S2: IR spectrum of complex **2**.

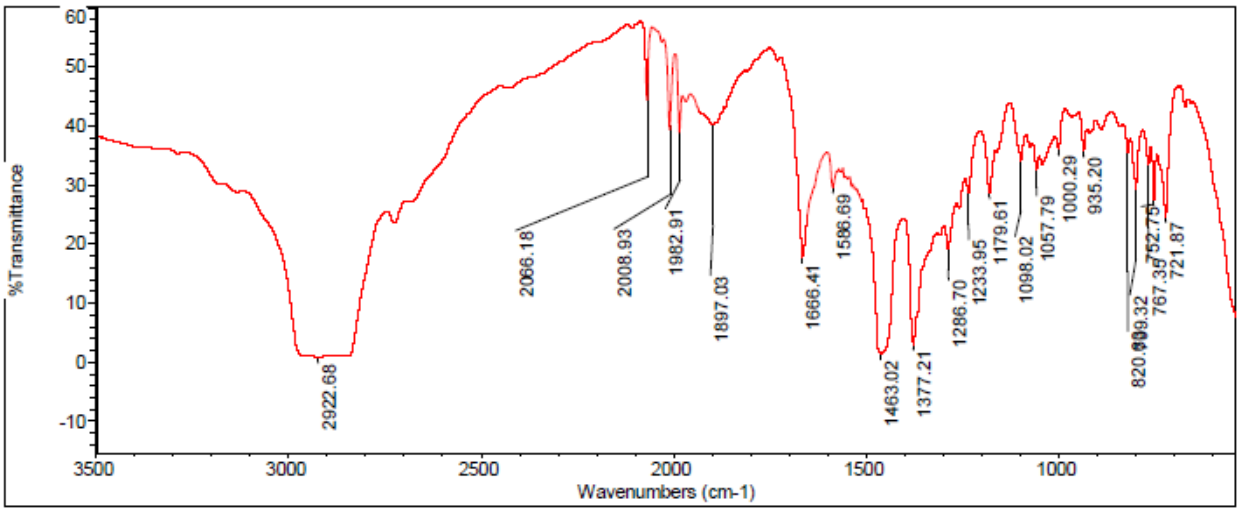

Figure S3: IR spectrum of the reaction mixture of complex **3**.

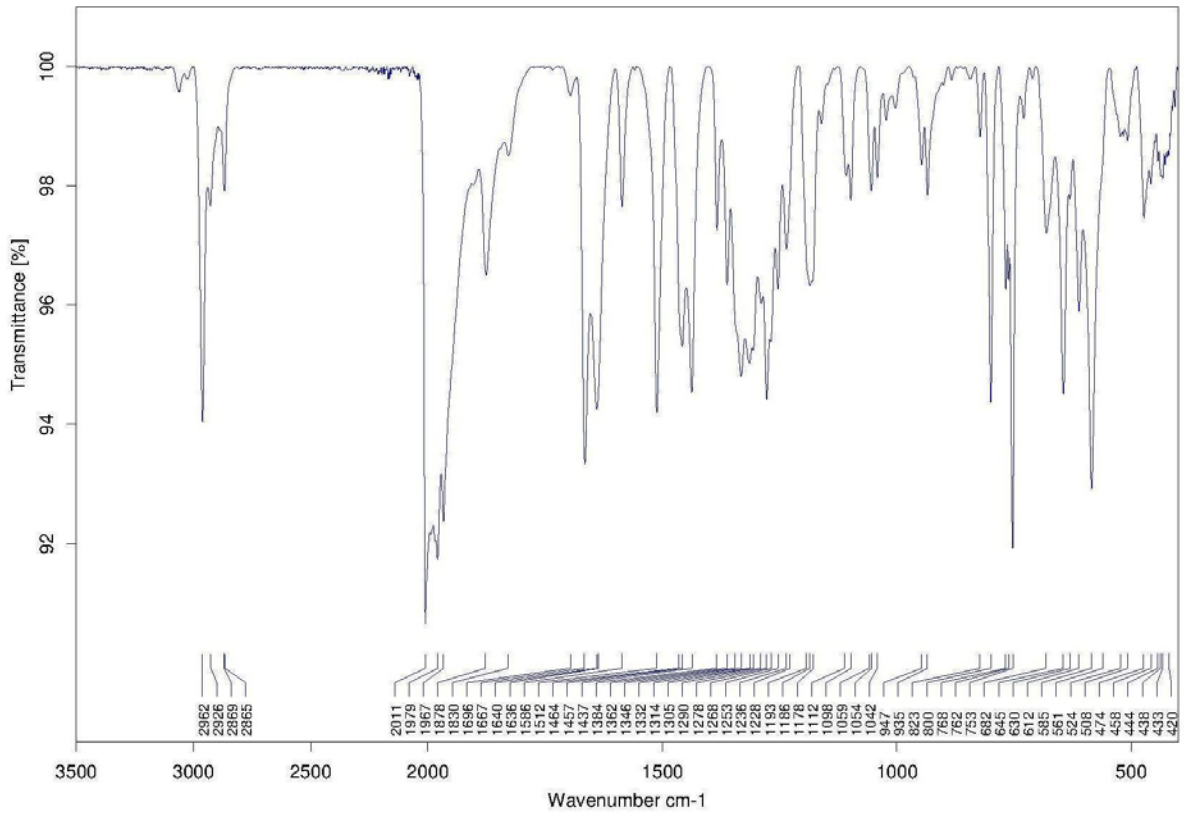

Figure S4: IR spectrum of complex **4**.

2. X-ray crystallography

A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the cold stream of a STOE IPDS 2 or a STOE StadiVari or Bruker SMART CCD diffractometer. All structures were solved by using the program SHELXS/T[1-2] and Olex2[3]. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F^2 by using the program SHELXL.[1-2] In each case, the locations of the largest peaks in the final difference Fourier map calculations, as well as the magnitude of the residual electron densities, were of no chemical significance.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. 1994647 (**1**), 1994648 (**2**), 1952438 (**3**), and 1994649 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

Refinement Details

The crystal structure of **4** contains a $[(\mu_3\text{-CO})_2Fe_3(CO)_9]^{2-}$ anion, which is disordered 50:50 over an inversion center in a 180° fashion. A correct parting in the space group $P2_1/n$ of the anions is not possible due to the symmetry. By solving and refining the structure in the space group P*n*, the values of R factors increase significantly, but parting is possible. To give the overall best quality the structure was solved and refined in $P2_1/n$ without parting (Figure S7 and S8).

2.1 Crystal Structures

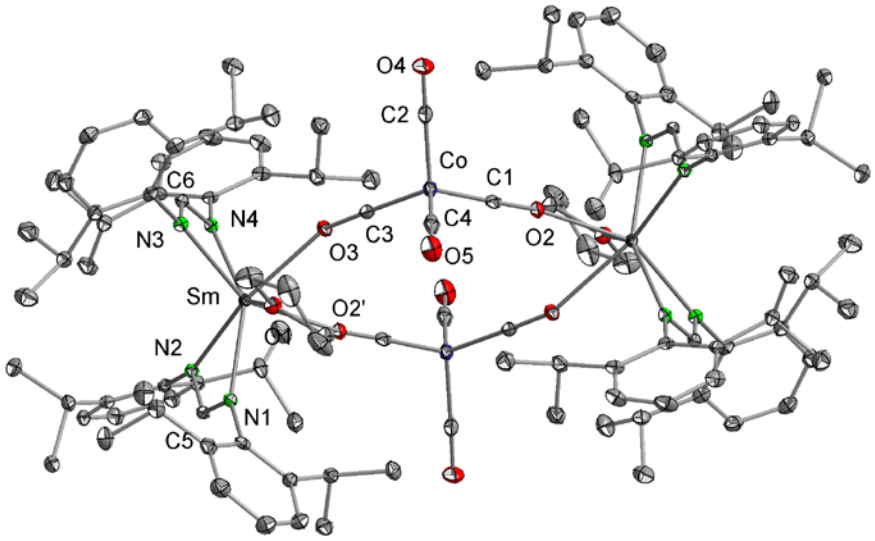

Figure S5: Molecular structure of **1** in the solid state with thermal ellipsoids at the 30% probability. H atoms are omitted for clarity. Atoms with the prime character in the atom labels (‘) are at equivalent positions. Selected bond distances (Å) and angles [°]: Sm-O1 2.422(2), Sm’-O2 2.488(3), Sm-O3 2.552(3), Sm-N1 2.431(3), Sm-N2 2.449(3), Sm-N3 2.409(3), Sm-N4 2.449(3), Co-C1 1.733(4), Co-C2 1.787(4), Co-C3 1.747(4), Co-C4 1.782(4), O2-C1 1.175(4), O3-C3 1.170(4), O4-C2 1.138(5), O5-C4 1.145(5), N1-C5 1.322(4), N2-C5 1.318(4), N3-C6 1.330(5), N4-C6 1.326(5); O2’-Sm-O3 67.27(8), N1-Sm-N2 55.35(9), N1-Sm-N4 143.10(10), C1-Co-C2 108.8(2), C1-Co-C3 116.1(2), C1-Co-C4 110.1(2), C3-Co-C2 109.7(2), C3-Co-C4 105.8(2), C4-Co-C2 105.8(2), N2-C5-N1 118.4(3), N4-C6-N3 120.3(3).

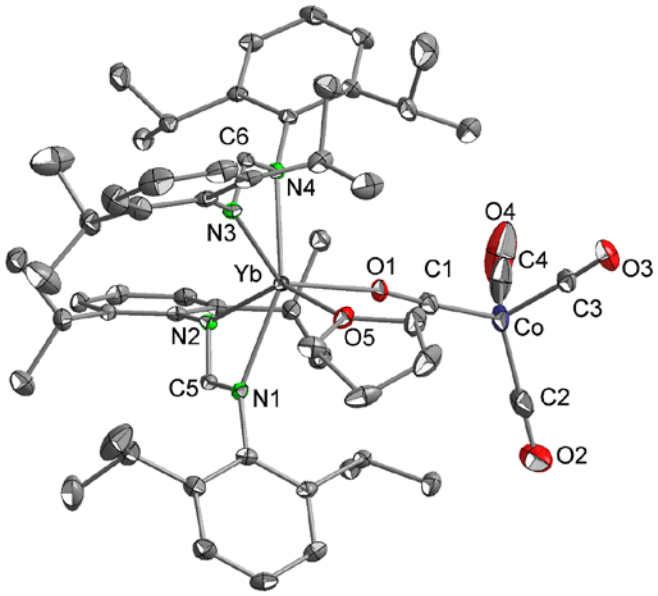

Figure S6: Molecular structure of **2** in the solid state with thermal ellipsoids at the 30% probability. H atoms are omitted for clarity. Selected bond distances (Å) and angles [°]: Yb-O1 2.248(2), Yb-O5 2.304(2), Yb-N1 2.307(2), Yb-N2 2.337(2), Yb-N3 2.292(2), Yb-N4 2.324(2), Yb-C5 2.697(3), Yb-C6 2.686(3), Co-C1 1.705(3), Co-C2 1.783(5), Co-C3 1.787(4), Co-C4 1.763(3), O1-C1 1.200(3), O2-C2 1.143(5), O3-C3 1.152(5), O4-C4 1.140(4), N1-C5 1.317(3), N2-C5 1.315(3), N3-C6 1.319(3), N4-C6 1.315(3); O1-Yb-O5 81.70(8), N1-Yb-N2 58.23(7), N1-Yb N4 99.80(8), N3-Yb-N1 112.08(8), N3-Yb-N2 114.88(8), C1-Co C2 111.8(2), C1-Co-C3 115.8(2), C1-Co-C4 109.6(2), C2-Co-C3 107.5(2), C4-Co-C2 104.6(2), C4-Co-C3 106.8(2).

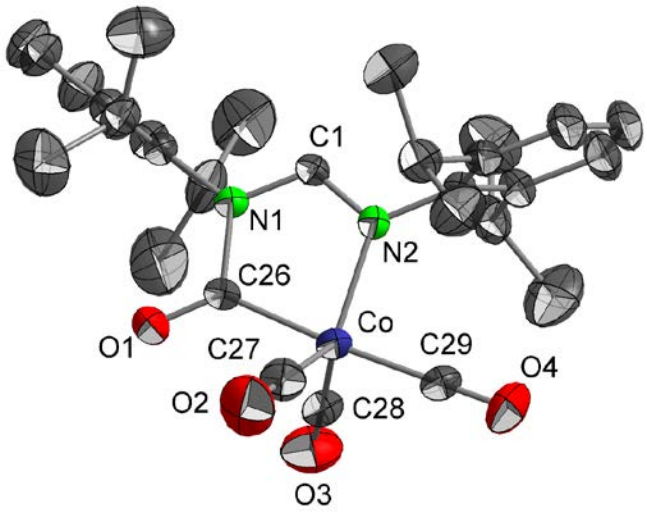

Figure S7: Molecular structure of **3** in the solid state with thermal ellipsoids at the 30% probability. Hydrogen atoms and solvent of crystallisation have been omitted for clarity. Selected bond lengths (Å) and angles [°]: Co1-N2 1.968(3), Co1-C26 1.930(4), Co1-C27 1.755(6), Co1-C28 1.755(6), Co1-C29 1.799(5), C1-N1 1.346(5), C1-N2 1.285(3), N1-C26 1.430(5), C26-O1 1.201(5), C27-O2 1.135(6), C28-O3 1.134(7), C29-O4 1.138(6); C26-Co1-N2 82.7(2), C27-Co1-N2 121.6(2), C28-Co1-N2 117.7(2), C29-Co1-N2 93.62(18), C26-Co1-C27 86.2(2), C26-Co1-C28 86.0(2), C26-Co1-C29 176.1(2), C27-Co1-C28 118.5(3), C28-Co1-C29 96.7(2), N1-C1-N2 118.3(4).

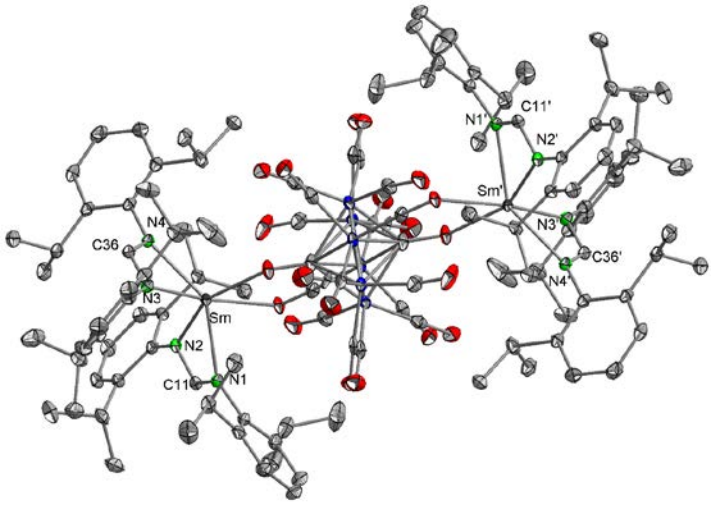

Figure S8: Molecular structure of **4** in the solid state with thermal ellipsoids at the 40% probability. H atoms are omitted for clarity. Atoms with the prime character in the atom labels (') are at equivalent positions. Selected bond distances (Å) and angles [°]: N1-Sm 2.409(2), N2-Sm 2.426(2), N3-Sm 2.381(2), N4-Sm 2.418(2), N1-C11 1.329(3), N2-C11 1.329(3), N3-C36 1.336(3), N4-C36 1.323(3); N1-C11-N2 117.87(2), N4-C36-N3 117.9(2), N1-Sm-N2 56.20(6), N1-Sm-N4 142.11(6), N3-Sm-N1 108.16(6), N3-Sm-N2 109.53(6), N3-Sm-N4 56.65(6). The bond lengths and angles for the $[(\mu_3\text{-CO})_2Fe_3(CO)_9]^{2-}$ moiety cannot be described precisely due to the disorder.

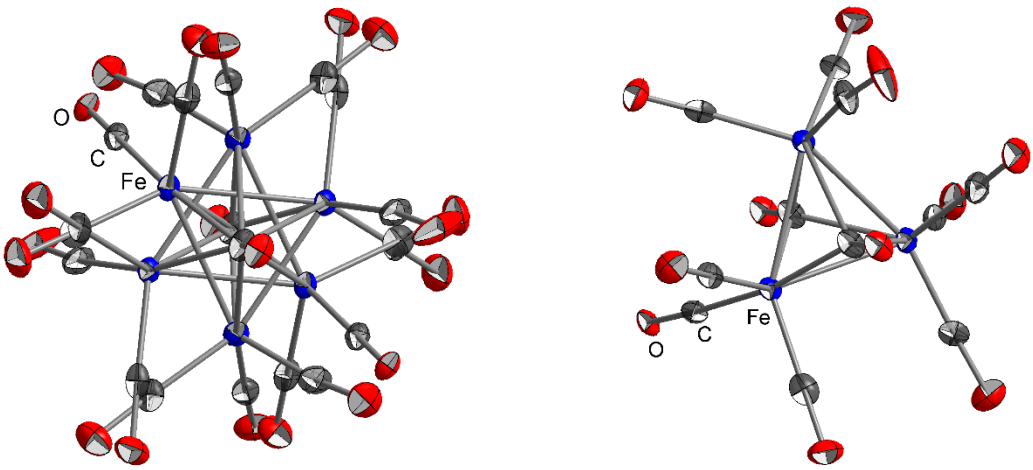

Figure S9: The cutout of the central $[(\mu_3\text{-CO})_2Fe_3(CO)_9]^{2-}$ of complex **4** with a view of complete disorder (left) and only one half for clarity (right).

2.2 Table S1: Crystal data and structure refinement

Compound	1	2	3* (thf)	4* (4 toluene)
Formula	$C_{116}H_{156}Co_2N_8O_{10}Sm_2$	$C_{58}H_{78}CoN_4O_5Yb$	$C_{33}H_{43}CoN_2O_5$	$C_{139}H_{172}Fe_3N_8O_{11}Sm_2$
$D_{calc.}$/ g cm^{-3}	1.361	1.345	1.165	1.318
μ/mm^{-1}	1.416	1.989	0.534	1.267
Formula Weight	2241.04	1143.21	606.62	2599.09
Colour	clear light yellow	orange	brown	clear red
Shape	plate	fragment	prism	block
Size/mm^3	0.20×0.13×0.03	0.29×0.19×0.08	0.40×0.25×0.10	0.33×0.28×0.24
T/K	100	150	298	100
Crystal System	monoclinic	triclinic	monoclinic	monoclinic
Space Group	$P2_1/n$	P-1	$P2_1/n$	$P2_1/n$
a/Å	11.942(2)	12.205(2)	11.1122(10)	17.4276(4)
b/Å	24.391(5)	14.110(3)	17.1592(17)	20.8564(3)
c/Å	18.910(4)	18.032(4)	18.425(2)	18.0530(4)
α/°		82.87(3)		
β/°	96.75(3)	77.96(3)	100.195(4)	93.692(2)
γ/°		68.54(3)		
V/Å^3	5470.2(19)	2822.5(12)	3457.7(6)	6548.2(2)
Z	2	2	4	2
Z'	0.5	1	1	0.5
Wavelength/Å	0.71073	0.71073	0.71073	0.71073
Radiation type	MoK_α	MoK_α	MoK_α	MoK_α
Θ_{min}/°	2.094	1.553	1.634	1.853
Θ_{max}/°	26.000	26.009	24.999	28.614
Measured Refl.	26613	21947	21302	67255
Independent Refl.	10715	11066	6021	15423
Reflections Used	8775	9247	2892	13087
R_{int}	0.0327	0.0260	0.1003	0.0671
Parameters	646	646	379	867
Restraints	0	0	63	0
Largest Peak	1.364	0.678	0.558	1.675
Deepest Hole	-1.022	-0.398	-0.524	-1.470
GooF	1.040	0.968	0.944	1.053
wR_2 (all data)	0.1008	0.0549	0.2308	0.0971
wR_2	0.0927	0.0526	0.1845	0.0942
R_1 (all data)	0.0533	0.0378	0.1341	0.0418
R_1	0.0390	0.0258	0.0675	0.0349

3 References

1. G. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112-122.
2. G. Sheldrick, *Acta Crystallogr., Sect. C*, 2015, **71**, 3-8.
3. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.