Electronic Supplementary Informations

For

Unprecedented dinuclear Robson type macrocyclic complexes having two +III metal ions in two compartments and the role of the diimino moiety on the stability of metal ion oxidation states

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Additional description of the structures of [$Co^{III}Co^{II}L^{Me–Me2pn}(N_3)_3$]·$2H_2O$ (5) and [$Co^{III}Co^{II}L^{Et–Me2pn}(N_3)_3$]·$H_2O$ (6) and their comparison with previously published compounds 5A[S1] and 6A[S2]

Selected bond lengths, bond angles and some other structural parameters for the Co^{III} centres in **5** and **6** are compared with each other and with those of the Co^{III} centres in the $Co^{III}Co^{III}$ compounds **1**–**4** in Table S2, while the individual bond lengths and bond angles are listed in Table S3. Except more asymmetry in the Co^{III}–azide bond distances in compound **5** (1.994 and 1.915 Å with asymmetry 0.079 Å), all other structural paremeters in the Co^{III} environment in **5** and **6** are similar to those in the Co^{III} environment in **1**–**4**. In fact, average Co^{III}–azide bond distance in **5** is also in the range of average Co^{III}–azide bond distances of other compounds. Hence, not only that the set of ligand atoms for the Co^{III} centres in **1**–**4** and **5**/**6** are identical but also the values of corresponding structural parameters involving the Co^{III} centres in the two sets of compounds are closely similar.

Structural parameters in the Co^{II} environment in **5** and **6** are listed in Table S4. Comparison of Co^{III}−phenoxo/imine bond distances in Table S2 and Co^{II}−phenoxo/imine bond distances in Table S4 reveal that former values are significantly smaller than the latter values, which arises due to difference in oxidation states of the metal ions. However, the difference between the Co^{III}−azide and Co^{II}−azide bond distances is not significant because of the significant shifting (0.417−0.638 Å) of cobalt(II) from the basal plane towards the axial atom. Clearly, coordination environment of cobalt(II) is highly distorted, which is also reflected in the *cisoid* (*ca*. 74.55−118.7°) and *transoid* angles (*ca*. 142.62−154.7°).

Crystallographic data of the $Co^{III}Co^{II}$ compounds **5** and **5A** are compared in Table S5. Crystal system and space group of both are the same, monoclinic and $P2_1/n$. The values of a (13.058 and 12.866 Å), b (20.926 and 20.357 Å), c (25.250 and 25.278 Å), and β (98.881 and 99.203°) are also not very different, from which it may seem that they are the same compound. However, there is some definite difference in their composition: $2H_2O$ in **5** versus $0.5CH_3CN·0.27H_2O$ in **5A**. It is worth mentioning that acetontrile moiety in **5A** was well assigned, while acetonitrile cannot be present in **5** because acetonitrile was not used at all in the synthesis of this latter compound. Hence, **5** and **5A** are definitely different compounds.

There are also some obvious differences in the structural parameters of the two compounds; *e. g.*, in the bond distances and more significantly in the bond angles involving Co^{II} centres (Table S6).

The $Co^{III}Co^{II}$ compounds **6** and **6A** are definitely different compounds in terms of space group ($P2_1/n$ versus $C2/c$) and the values of unit cell parameters (a, b, c, β: 13.546, 20.580, 25.681 Å and 101.222° versus 32.855, 12.339, 19.200 Å and 113.975°; Table S5) as well in terms of the solvent of crystallization (one water versus one acetonitrile). In the synthesis of **6** also (as in **5**), acetonitrile was not used. As **6** contains two units and **6A** contains one unit and as the Co^{II} centre in **6A** is disordered, it is not logical to comment on the comparative structural parameters (Table S6) of the Co^{II} centres of the two compounds (as already mentioned, Co^{III} environments are closely similar in the $Co^{III}Co^{III}$ and $Co^{III}Co^{II}$ compounds).

Table S1 Selected structural parameters (distances in Å and angles in °) of **1**–**4**

	1	**2**	**3**	**4**
Co1–O1	1.939(4)	1.948(3)	1.934(4)	1.946(4)
Co1–O2	1.948(4)	1.945(3)	1.944(4)	1.951(4)
Co1–N1	1.907(5)	1.914(4)	1.898(5)	1.907(5)
Co1–N2	1.905(5)	1.905(4)	1.893(5)	1.908(5)
Co1–N5	1.940(6)	1.940(4)	1.927(6)	1.949(6)
Co1–N8	1.962(6)	1.950(5)	1.951(5)	1.963(6)
Co2–O1	1.958(4)	1.959(3)	1.938(4)	1.959(4)
Co2–O2	1.935(4)	1.944(3)	1.935(4)	1.949(4)
Co2–N3	1.903(5)	1.893(4)	1.885(5)	1.904(5)
Co2–N4	1.912(5)	1.915(5)	1.894(4)	1.927(6)
Co2–N11	1.944(6)	1.949(5)	1.938(5)	1.945(6)
Co2–N14	1.956(6)	1.971(6)	1.934(5)	1.988(6)
Co1···Co2	3.013	3.010	2.984	3.021
O1–Co1–N2	171.0(2)	171.54(16)	171.29(19)	171.0(2)
O2–Co1–N1	171.0(2)	171.10(17)	171.42(18)	171.4(2)
N5–Co1–N8	178.1(2)	178.5(2)	178.5(2)	178.9(3)
N5–Co1–O1	92.7(2)	92.89(17)	91.6(2)	92.7(2)
N5–Co1–O2	89.1(2)	89.06(16)	89.4(2)	89.5(2)
N5–Co1–N1	89.9(2)	89.85(19)	91.1(2)	89.6(2)
N5–Co1–N2	87.0(2)	87.51(19)	88.1(2)	88.0(2)
N8–Co1–O1	88.7(2)	88.57(19)	89.55(19)	88.2(2)
N8–Co1–O2	89.9(2)	91.01(18)	89.8(2)	91.2(2)
N8–Co1–N1	91.3(2)	90.3(2)	89.9(2)	89.8(3)
N8–Co1–N2	91.3(2)	91.0(2)	90.6(2)	91.2(2)
O1–Co1–O2	78.55(16)	79.01(13)	79.22(15)	78.67(17)
O1–Co1–N1	92.6(2)	92.23(18)	92.20(19)	92.9(2)
O2–Co1–N2	92.50(19)	92.54(16)	92.07(19)	92.41(19)
N1–Co1–N2	96.4(2)	96.23(19)	96.5(2)	96.1(2)
O1–Co2–N3	171.2(2)	171.58(17)	171.71(18)	171.1(2)
O2–Co2–N4	170.7(2)	170.36(17)	171.93(17)	170.8(2)
N11–Co2–N14	176.4(2)	178.2(2)	177.5(2)	176.1(3)
N11–Co2–O1	89.6(2)	90.64(17)	89.86(19)	90.9(2)
N11–Co2–O2	91.8(2)	93.11(18)	91.94(19)	93.5(2)
N11–Co2–N3	89.2(2)	90.2(2)	91.2(2)	90.1(2)
N11–Co2–N4	87.7(2)	88.8(2)	88.1(2)	87.9(2)
N14–Co2–O1	89.8(2)	89.50(19)	88.3(2)	88.8(2)
N14–Co2–O2	91.7(2)	88.67(19)	89.38(19)	90.3(2)
N14–Co2–N3	91.9(2)	89.9(2)	90.8(2)	90.7(2)
N14–Co2–N4	88.7(2)	89.4(2)	90.3(2)	88.3(3)
O1–Co2–O2	78.40(16)	78.76(13)	79.35(16)	78.40(17)
O1–Co2–N4	92.3(2)	91.77(17)	92.57(18)	92.4(2)
O2–Co2–N3	92.88(19)	92.83(16)	92.39(18)	92.7(2)
N3–Co2–N4	96.4(2)	96.61(19)	95.7(2)	96.4(2)
Co1–O1–Co2	101.25(17)	100.78(15)	100.82(17)	101.36(18)
Co1–O2–Co2	101.78(16)	101.43(14)	100.58(17)	101.57(18)

Table S2 Comparison of selected structural parameters (distances in Å and angles in °) of the Co^{III} centres in **1–6**

		Derived from $H_2L^{Me–pn}$		Derived from $H_2L^{Et–pn}$			Derived from $H_2L^{Me–Me2pn}$	Derived from $H_2L^{Et–Me2pn}$
		1	**2**	**3**	**4**		**5**	**6**
Co^{III}–O(phenoxo)	Co1	1.939(4), 1.948(4)	1.948(3), 1.945(3)	1.934(4), 1.944(4)	1.946(4), 1.951(4)	Co2(Unit-I)	1.939(4), 1.923(4)	1.927(3), 1.927(3)
	Co2	1.958(4), 1.935(4)	1.959(3), 1.944(3)	1.938(4), 1.935(4)	1.959(4), 1.949(4)	Co4A(Unit-II)[c]	1.949(4), 1.927(4)	1.920(3), 1.918(3)
	Average	1.945	1.949	1.938	1.951	Average	1.934	1.923
Co^{III}–N(imine)	Co1	1.907(5), 1.905(5)	1.914(4), 1.905(4)	1.898(5), 1.893(5)	1.907(5), 1.908(5)	Co2(Unit-I)	1.912(5), 1.911(6)	1.914(4), 1.914(4)
	Co2	1.903(5), 1.912(5)	1.893(4), 1.915(5)	1.885(5), 1.894(4)	1.904(5), 1.927(6)	Co4A(Unit-II)[c]	1.895(5), 1.920(5)	1.917(4), 1.898(4)
	Average	1.907	1.907	1.892	1.912	Average	1.910	1.911
Co^{III}–N(azide)	Co1	1.940(6), 1.962(6)	1.940(4), 1.950(5)	1.927(6), 1.951(5)	1.949(6), 1.963(6)	Co2(Unit-I)	1.915(7), 1.994(6)	1.943(4), 1.962(4)
	Co2	1.944(6), 1.956(6)	1.949(5), 1.971(6)	1.938(5), 1.934(5)	1.945(6), 1.988(6)	Co4A(Unit-II)[c]	1.959(6), 1.956(6)	1.945(5), 1.973(5)
	Average	1.951	1.952	1.938	1.961	Average	1.956	1.956
Cisoid angles' range for Co^{III} centre	Co1	78.55(16) –96.4(2)	79.01(13) –96.23(19)	79.22(15) –96.5(2)	78.67(17) –96.1(2)	Co2(Unit-I)	79.24(19) –95.3(2)	80.54(12) –94.99(16)
	Co2	78.40(16) –96.4(2)	78.76(13) –96.61(19)	79.35(16) –95.7(2)	78.40(17) –96.4(2)	Co4A(Unit-II)[c]	80.29(17) –95.5(2)	80.53(13) –95.21(18)
Transoid angles' range for Co^{III} centre	Co1	171.0(2) –178.1(2)	171.10(17) –178.5(2)	171.29(19) –178.5(2)	171.0(2) –178.9(3)	Co2(Unit-I)	171.8(2) –177.7(3)	172.64(14) –178.12(17)
	Co2	170.7(2) –176.4(2)	170.36(17) –178.2(2)	171.71(18) –177.5(2)	170.8(2) –176.1(3)	Co4A(Unit-II)[c]	171.6(2) –177.7(3)	172.39(15) –177.76(19)
d_{av}[a]	Co1	0.011	0.017	0.003	0.017	Co2(Unit-I)	0.010	0.011
	Co2	0.008	0.011	0.005	0.006	Co4A(Unit-II)[c]	0.002	0.005
$d_{Co^{III}}$[a]	Co1	0.013	0.009	0.0002	0.005	Co2(Unit-I)	0.009	0.004
	Co2	0.017	0.020	0.008	0.016	Co4A(Unit-II)[c]	0.015	0.005
Co^{III}–O(phenoxo)–Co^{III}		101.25(17), 101.78(16)	100.78(15), 101.43(14)	100.82(17), 100.58(17)	101.36(18), 101.57(18)		–	–
Co^{III}–O(phenoxo)–Co^{II}		–	–	–	–	Unit-I	101.3(2), 101.8(2)	101.37(13), 100.59(12)
						Unit-II	100.16(18), 100.56(19)	100.04(14), 99.80(13)
Co^{III}···Co^{III}		3.013	3.010	2.984	3.021		–	–
Co^{III}···Co^{II}		–	–	–	–	Unit-I	3.066	3.072
						Unit-II	3.027	3.038
δ (phenyl···phenyl)[b]		53.60	55.51	63.03	55.27		46.03/61.24	48.74/64.35

[a] d_{av} and $d_{Co^{III}}$ are the average deviation of the constituting atoms and displacement of the metal centres from the corresponding least-squares N(imine)$_2$O(phenoxo)$_2$ basal plane.

[b] Dihedral angle between two phenyl rings. [c] Co4 centre in compound **5** is disordered over two sites with occupancies 0.90 and 0.10; structural parameters of the site of major occupancy are listed here.

Table S3 Selected structural parameters (distances in Å and angles in °) of **5** and **6**

Unit	Compound		Unit	Compound	
I	**5**	**6**	II	**5**[a]	**6**[b]
Co1–O1	2.024(5)	2.042(3)	Co3/Co3A–O3	1.998(4)	2.043(3)
Co1–O2	2.028(4)	2.065(3)	Co3/Co3A–O4	2.008(4)	2.052(3)
Co1–N1	2.022(7)	2.036(4)	Co3/Co3A–N14	2.002(6)	2.048(4)
Co1–N2	2.023(7)	2.035(4)	Co3/Co3A–N15	1.987(5)	2.078(4)
Co1–N5	1.972(8)	1.967(5)	Co3/Co3A–N18	2.020(10)	1.900(7)
Co2–O1	1.939(4)	1.927(3)	Co4/Co4A–O3	1.949(4)	1.920(3)
Co2–O2	1.923(4)	1.927(3)	Co4/Co4A–O4	1.927(4)	1.918(3)
Co2–N3	1.912(5)	1.914(4)	Co4/Co4A–N16	1.895(5)	1.917(4)
Co2–N4	1.911(6)	1.914(4)	Co4/Co4A–N17	1.920(5)	1.898(4)
Co2–N8	1.915(7)	1.943(4)	Co4/Co4A–N21	1.959(6)	1.945(5)
Co2–N11	1.994(6)	1.962(4)	Co4/Co4A–N24/N24A	1.956(6)	1.973(5)
Co1···Co2	3.066	3.072	Co3/Co3A···Co4/Co4A	3.027	3.038
O1–Co1–N2	149.0(2)	147.32(15)	O3– Co3/Co3A–N15	154.3(2)	142.62(17)
O2–Co1–N1	153.0(2)	151.44(16)	O4– Co3/Co3A–N14	154.7(2)	143.29(16)
N5–Co1–O1	111.4(3)	112.08(18)	N18– Co3/Co3A–O3	106.0(3)	118.7(2)
N5–Co1–O2	104.2(3)	107.30(16)	N18–Co3/Co3A–O4	107.8(3)	116.2(2)
N5–Co1–N1	101.7(3)	100.54(19)	N18– Co3/Co3A–N14	96.5(3)	100.5(2)
N5–Co1–N2	98.2(3)	99.6(2)	N18– Co3/Co3A–N15	99.0(3)	98.5(3)
O1–Co1–O2	74.88(18)	74.68(11)	O3–Co3/Co3A–O4	77.18(16)	74.55(12)
O1–Co1–N1	88.9(3)	89.23(15)	O3–Co3/Co3A–N14	89.5(2)	87.09(16)
O2–Co1–N2	89.6(2)	88.69(14)	O4–Co3/Co3A–N15	89.8(2)	86.45(15)
N1–Co1–N2	94.0(3)	92.93(17)	N14–Co3/Co3A–N15	93.5(2)	89.73(17)
O1–Co2–N3	172.1(2)	172.85(14)	O3– Co4/Co4A–N16	173.1(2)	172.39(15)
O2–Co2–N4	171.8(2)	172.64(14)	O4– Co4/Co4A–N17	171.6(2)	172.91(16)
N8–Co2–N11	177.7(3)	178.12(17)	N21– Co4/Co4A–N24/N24A	177.3(3)	177.76(19)
N8–Co2–O1	91.7(2)	91.68(14)	N21– Co4/Co4A–O3	92.0(2)	87.83(17)
N8–Co2–O2	91.1(2)	90.02(16)	N21– Co4/Co4A–O4	87.5(2)	91.12(17)
N8–Co2–N3	88.3(3)	89.20(16)	N21– Co4/Co4A–N16	86.9(2)	92.27(19)
N8–Co2–N4	90.3(3)	89.74(17)	N21– Co4/Co4A–N17	91.9(2)	89.20(19)
N11–Co2–O1	90.6(2)	89.75(14)	N24/N24A– Co4/Co4A–O3	90.6(2)	91.00(17)
N11–Co2–O2	89.1(2)	89.02(15)	N24/N24A– Co4/Co4A–O4	92.4(2)	90.56(17)
N11–Co2–N3	89.4(3)	89.23(16)	N24/N24A– Co4/Co4A–N16	90.4(3)	89.14(19)
N11–Co2–N4	89.8(3)	91.43(16)	N24/N24A– Co4/Co4A–N17	88.6(2)	88.95(19)
O1–Co2–O2	79.24(19)	80.54(12)	O3– Co4/Co4A–O4	80.29(17)	80.53(13)
O1–Co2–N4	92.6(2)	92.11(14)	O3– Co4/Co4A–N17	91.4(2)	92.40(16)
O2–Co2–N3	92.9(2)	92.36(14)	O4– Co4/Co4A–N16	92.8(2)	91.86(15)
N3–Co2–N4	95.3(2)	94.99(16)	N16– Co4/Co4A–N17	95.5(2)	95.21(18)
Co1–O1–Co2	101.3(2)	101.37(13)	Co3/Co3A–O3–Co4/Co4A	100.16(18)	100.04(14)
Co1–O2–Co2	101.8(2)	100.59(12)	Co3/Co3A–O4–Co4/Co4A	100.56(19)	99.80(13)

[a] Co4 centre in compound **5** is disordered over two sites with occupancies 0.90 and 0.10 and coordinated azide nitrogen atom N24 in compound **5** is disordered over two sites with occupancies 0.80 and 0.20; structural parameters of the site of major occupancy are listed here.

[b] Co3 centre in compound **6** is disordered over two sites with occupancies 0.80 and 0.20; structural parameters of the site of major occupancy are listed here.

Table S4 Comparison of selected structural parameters (distances in Å and angles in °) of the Co^{II} centre in **5** and **6**

		Derived from H$_2$L$^{Me–Me2pn}$	Derived from H$_2$L$^{Et–Me2pn}$
		5	**6**
Co^{II}–O(phenoxo)	Co1(Unit-I)	2.024(5), 2.028(4)	2.042(3), 2.065(3)
	Co3/Co3A(Unit-II)^{b}	1.998(4), 2.008(4)	2.043(3), 2.052(3)
	Average	2.014	2.051
Co^{II}–N(imine)	Co1(Unit-I)	2.022(7), 2.023(7)	2.036(4), 2.035(4)
	Co3/Co3A(Unit-II)^{b}	2.002(6), 1.987(5)	2.048(4), 2.078(4)
	Average	2.008	2.049
Co^{II}–N(azide)	Co1(Unit-I)	1.972(8)	1.967(5)
	Co3/Co3A(Unit-II)^{b}	2.020(10)	1.900(7)
	Average	1.996	1.934
Cisoid angles' range for Co^{II} centre	Co1(Unit-I)	74.88(18) –111.4(3)	74.68(11) –112.08(18)
	Co3/Co3A(Unit-II)^{b}	77.18(16) –107.8(3)	74.55(12) –118.7(2)
Transoid angles' range for Co^{II} centre	Co1(Unit-I)	149.0(2) –153.0(2)	147.32(15) –151.44(16)
	Co3/Co3A(Unit-II)^{b}	154.3(2) –154.7(2)	142.62(17) –143.29(16)
d_{av}^{a}	Co1(Unit-I)	0.039	0.034
	Co3/Co3A(Unit-II)^{b}	0.003	0.006
d_{Co}^{IIa}	Co1(Unit-I)	0.475	0.513
	Co3/Co3A(Unit-II)^{b}	0.417	0.638

[a] d_{av} and d_{Co}^{II} are the average deviation of the constituting atoms and displacement of the metal centres from the corresponding least-squares N(imine)$_2$O(phenoxo)$_2$ basal plane.

[b] Co3 centre in compound **6** is disordered over two sites with occupancies 0.80 and 0.20; structural parameters of the site of major occupancy are listed here.

Table S5 Crystallographic data for **5**, **5A**,[S1] **6** and **6A**[S2]

	5	**5A(120 K)**[a]	**5A (296 K)**[a]	**6**	**6A**
Empirical formula	$C_{28}H_{38}N_{13}O_4Co_2$	$C_{29}H_{36.04}N_{13.5}O_{2.27}Co_2$	$C_{29}H_{36.04}N_{13.5}O_{2.27}Co_2$	$C_{30}H_{40}N_{13}O_3Co_2$	$C_{32}H_{41}N_{14}O_2Co_2$
Formula weight	738.58	727.94	727.93	748.61	771.64
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$C2/c$
a /Å	13.058(6)	12.8658(3)	12.9718(16)	13.5457(10)	32.855(12)
b /Å	20.926(10)	20.3574(3)	20.614(3)	20.5805(16)	12.339(4)
c /Å	25.250(12)	25.2780(4)	25.402(3)	25.681(2)	19.200(7)
α /°	90.00	90.00	90.00	90.00	90.00
β /°	98.881(6)	99.203(2)	99.677(2)	101.222(3)	113.975(5)
γ /°	90.00	90.00	90.00	90.00	90.00
V /Å^3	6816(6)	6535.4(2)	6696.0(15)	7022.4(9)	7112(4)
Z	8	8	8	8	8
ρ_{calcd} /g cm^{-3}	1.439	1.480	1.444	1.416	1.441
λ (Mo K$_\alpha$)/Å	0.71073	0.71073	0.71073	0.71073	0.71073
μ /mm^{-1}	1.027	1.067	1.041	0.996	0.985
T /K	296(2)	120(2)	296(2)	296(2)	100(2)
F(000)	3064	3014	3014	3112	3208
2θ range for data collection/°	2.54–50.00	5.12–52.74	2.56–50.20	2.56–50.22	2.72–50.88
Index ranges	$-15 \le h \le 15$	$-16 \le h \le 16$	$-15 \le h \le 15$	$-16 \le h \le 15$	$-39 \le h \le 39$
	$-24 \le k \le 22$	$-25 \le k \le 24$	$-23 \le k \le 24$	$-24 \le k \le 23$	$-14 \le k \le 14$
	$-30 \le l \le 30$	$-31 \le l \le 17$	$-29 \le l \le 27$	$-30 \le l \le 30$	$-23 \le l \le 23$
No. measured reflections	46160	36265	46055	77903	34359
No. independent reflections	11967	13340	11871	12487	6533
R_{int}	0.0550	0.0658	0.0758	0.0589	0.0931
Goodness-of-fit on F^2, S	1.029	0.773	0.991	1.060	1.016
R_1[b], wR_2[c] ($I > 2\sigma(I)$)	0.0837, 0.1968	0.0412, 0.0583	0.0505, 0.1062	0.0580, 0.1852	0.0520, 0.1282
R_1[b], wR_2[c] (all data)	0.1246 , 0.2162	0.0912, 0.0633	0.0891, 0.1181	0.0892, 0.2270	0.0878, 0.1478

[a] Structure of **5A** was determined previously at 120 K,[S1] while Structure of **5** in this investigation has been determined at 296 K . Therefore to compare the parameters between **5** and **5A**, structure of **5A** has been redetermined in this investigation at 296 K. While $0.5CH_3CN\cdot0.27H_2O$ in **5A** could be properly assigned from 120 K data, those could not be properly assigned from 296 K data. Therefore for 296 K data, these solvent molecules were eliminated by using the SQUEEZE facility of PLATON to improve the refinement.[31e] Electron count per unit cell for the eliminated solvent is 106, indicating the presence of $0.5CH_3CN\cdot0.27H_2O$ solvent molecules per dinuclear unit (Z=8).

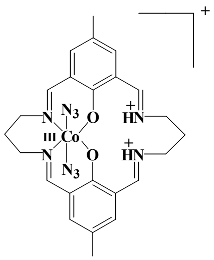
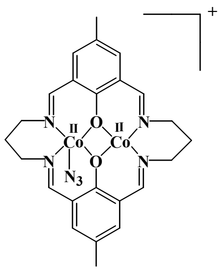
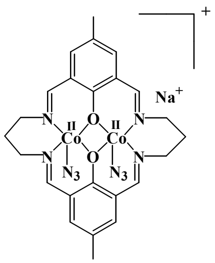
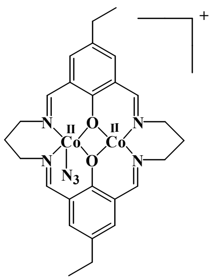
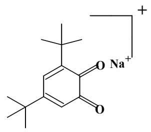
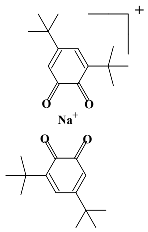
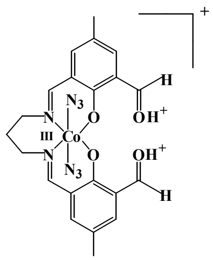
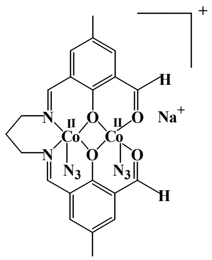
[b] $R_1 = [\sum||F_o| - |F_c||/\sum|F_o|]$. [c] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

Table S6 Comparison of selected structural parameters (distances in Å and angles in °) of the Co^{III} and Co^{II} centres in **5**, **5A**,[S1] **6** and **6A**[S2]

	Derived from $H_2L^{Me–Me2pn}$						Derived from $H_2L^{Et–Me2pn}$		
	5		**5A(120 K)**[d]		**5A(296 K)**[d]		**6**		**6A**
Unit	I	II	I	II	I	II	I	II	–
Co^{II}–O(phenoxo)	2.024(5), 2.028(4)	1.998(4), 2.008(4)	2.0313(19), 2.077(2)	2.0293(19), 2.062(2)	2.070(2), 2.050(2)	2.040(2), 2.061(2)	2.042(3), 2.065(3)	2.043(3), 2.052(3)	2.042(3), 2.076(3)
Co^{II}–N(imine)	2.022(7), 2.023(7)	2.002(6), 1.987(5)	2.035(2), 2.058(2)	2.018(3), 2.033(2)	2.036(3), 2.056(3)	2.040(3), 2.030(3)	2.036(4), 2.035(4)	2.048(4), 2.078(4)	2.039(4), 2.059(3)
Co^{II}–N(azide)	1.972(8)	2.020(10)	1.984(3)	1.986(3)	1.957(4)	1.973(4)	1.967(5)	1.900(7)	1.978(4)
Cisoid angles' range for Co^{II} centre	74.88(18) – 111.4(3)	77.18(16) – 107.8(3)	75.28(7) – 114.17(10)	74.82(8) – 112.01(9)	75.00(9) – 115.55(14)	74.59(9) – 111.90(13)	74.68(11) – 112.08(18)	74.55(12) – 118.7(2)	75.39(10) – 113.05(15)
Transoid angles' range for Co^{II} centre	149.0(2) – 153.0(2)	154.3(2) – 154.7(2)	145.48(10) – 147.38(9)	147.83(9) – 154.32(10)	145.66(11) – 146.17(11)	147.77(12) – 152.46(12)	147.32(15) – 151.44(16)	142.62(17) – 143.29(16)	145.53(12) – 150.01(12)
$d_{av}(Co^{II})$[a]	0.039	0.003	0.009	0.055	0.0005	0.042	0.034	0.006	0.036
$d_{Co}{}^{II}$[a]	0.475	0.417	0.572	0.476	0.581	0.496	0.513	0.638	0.551
Co^{III}–O(phenoxo)	1.939(4), 1.923(4)	1.949(4), 1.927(4)	1.9178(18), 1.928(2)	1.934(2) 1.9343(18)	1.919(2), 1.926(2)	1.936(2), 1.931(2)	1.927(3), 1.927(3)	1.920(3), 1.918(3)	1.929(3), 1.933(3)
Co^{III}–N(imine)	1.912(5), 1.911(6)	1.895(5), 1.920(5)	1.900(2), 1.910(2)	1.906(2), 1.912(2)	1.905(3), 1.903(3)	1.910(3), 1.914(3)	1.914(4), 1.914(4)	1.917(4), 1.898(4)	1.911(3), 1.915(3)
Co^{III}–N(azide)	1.915(7), 1.994(6)	1.959(6), 1.956(6)	1.941(3), 1.969(2)	1.929(3), 1.977(3)	1.938(3), 1.960(3)	1.919(4), 1.976(3)	1.943(4), 1.962(4)	1.945(5), 1.973(5)	1.947(4), 1.969(3)
Cisoid angles' range for Co^{III} centre	79.24(19) – 95.3(2)	80.29(17) – 95.5(2)	81.45(8) – 95.34(11)	79.96(8) – 95.21(10)	81.43(10) – 95.55(13)	79.98(10) – 95.42(13)	80.54(12) – 94.99(16)	80.53(13) – 95.21(18)	81.41(11) – 95.27(14)
Transoid angles' range for Co^{III} centre	171.8(2) – 177.7(3)	171.6(2) – 177.3(3)	173.03(10) – 176.57(10)	172.19(9) – 178.45(12)	172.76(12) – 177.00(14)	172.08(12) – 178.01(15)	172.64(14) – 178.12(17)	172.39(15) – 177.76(19)	172.89(13) – 178.30(15)
$d_{av}(Co^{III})$[b]	0.010	0.002	0.002	0.004	0.003	0.006	0.011	0.005	0.008
$d_{Co}{}^{III}$[b]	0.009	0.015	0.001	0.007	0.006	0.002	0.004	0.005	0.004
Co^{II}–O(phenoxo)–Co^{III}	101.3(2), 101.8(2)	100.16(18), 100.56(19)	99.20(8), 100.47(8)	100.65(9), 101.82(9)	99.69(10), 100.17(10)	100.95(11), 101.53(11)	101.37(13), 100.59(12)	100.04(14), 99.80(13)	99.74(12), 100.82(12)
Co^{II}···Co^{III}	3.066	3.027	3.04395(7)	3.07690(3)	3.050	3.081	3.072	3.038	3.064
δ (phenyl···phenyl)[c]	46.03	61.24	64.05	45.36	62.71	44.60	48.74	64.35	69.96

[a] $d_{av}(Co^{II})$ and $d_{Co}{}^{II}$ are the average deviation of the constituting atoms and displacement of the Co^{II} centre from the least-squares N(imine)$_2$O(phenoxo)$_2$ basal plane containing the Co^{II} centre. [b] $d_{av}(Co^{III})$ and $d_{Co}{}^{III}$ are the average deviation of the constituting atoms and displacement of the Co^{III} centre from the least-squares N(imine)$_2$O(phenoxo)$_2$ basal plane containing the Co^{III} centre. [c] Dihedral angle between two phenyl rings. [d] The structure of **5A** at 120 K was reported in *Inorg*. *Chim*. *Acta*, 2014, **412**, 38, while the structure at 296 K has been determined in the present investigation.

Table S7 The composition, empirical formula, peak position and relative peak intensity of the species in the ESI-MS positive spectra of **1**, **3**, **1** with 3,5-DTBCH$_2$ and **3** with 3,5-DTBCH$_2$ in MeCN

		I	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**
Species illustration									
Species formula		$[\mathrm{Co^{III}(L^{Me\text{–}pn}H_2)(N_3)_2}]^+$	$[\mathrm{Co^{II}Co^{II}L^{Me\text{-}pn}N_3}]^+$	$[\mathrm{Co^{II}Co^{II}L^{Me\text{-}pn}(N_3)_2}$ $+\mathrm{Na^+}]^+$	$[\mathrm{Co^{II}Co^{II}L^{Et\text{–}pn}N_3}]^+$	[(3,5-DTBQ)Na]$^+$	[(3,5-DTBQ)$_2$Na]$^+$	$[\mathrm{Co^{III}L^1(N_3)_2{+}2H^+}]^+$	$[\mathrm{Co^{II}Co^{II}L^1(N_3)_2{+}\ Na^+}]^+$
Empirical formula; m/z^a		$C_{24}H_{28}N_{10}O_2Co$; 547	$C_{24}H_{26}N_7O_2Co_2$; 562	$C_{24}H_{26}N_{10}O_2Co_2Na$; 627	$C_{26}H_{30}N_7O_2Co_2$; 590	$C_{14}H_{20}O_2Na$; 243	$C_{28}H_{40}O_4Na$; 463	$C_{21}H_{22}N_8O_4Co$; 509	$C_{21}H_{20}N_8O_4Co_2Na$; 589
Relative peak intensity	**1**	100%	73%	45%	– – – – – – – – – – –	– – – – – – –	– – – – – – –	– – – – – – – – – – –	– – – – – – – – – – –
	3	– – – – – – – – – – – –	– – – – – – – – – – – –	– – – – – – – – – – – –	100%	– – – – – – –	– – – – – – –	– – – – – – – – – – –	– – – – – – – – – – –
	1+3,5-DTBCH$_2$	22% (after 5 min)	– – – – – – – – – – – –	– – – – – – – – – – – – –	– – – – – – – – – – –	28% (after 5 min) 100% after 15 min)	14% (after 5 min) 40% (after 15 min)	10% (after 5 min) 8% (after 15 min)	10% (after 15 min)
	3+3,5-DTBCH$_2$	– – – – – – – – – – – –	– – – – – – – – – – – –	– – – – – – – – – – – – –	– – – – – – – – – – –	100% (after 5 min) 100% (after 15 min)	42% (after 5 min) 95% (after 15 min)	– – – – – – – – – – –	– – – – – – – – – – –

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[a] m/z values quoted in this table are for the major peak in the isotope pattern.

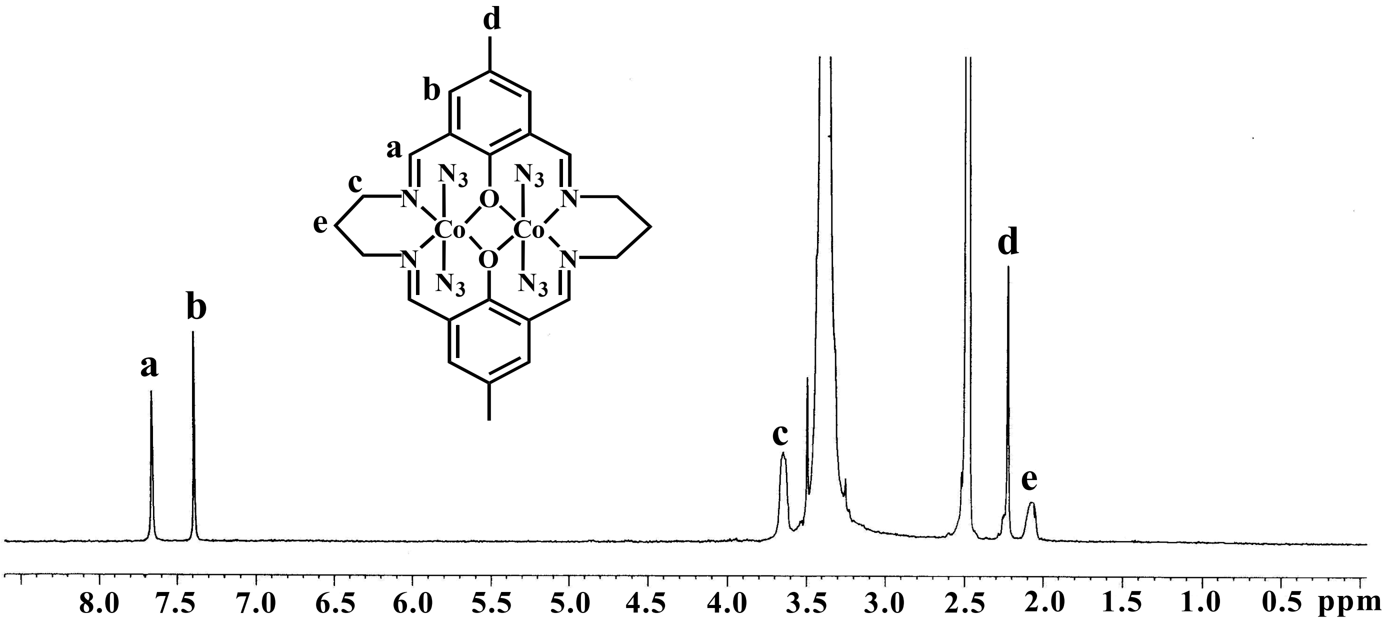


Fig. S1 ^{1}H NMR spectrum of $[\mathrm{Co^{III}Co^{III}L^{Me\text{–}pn}(N_3)_4}]\cdot 4H_2O$ (**2**; the sample with which spectrum was recorded contains one instead of four water of crystallization).

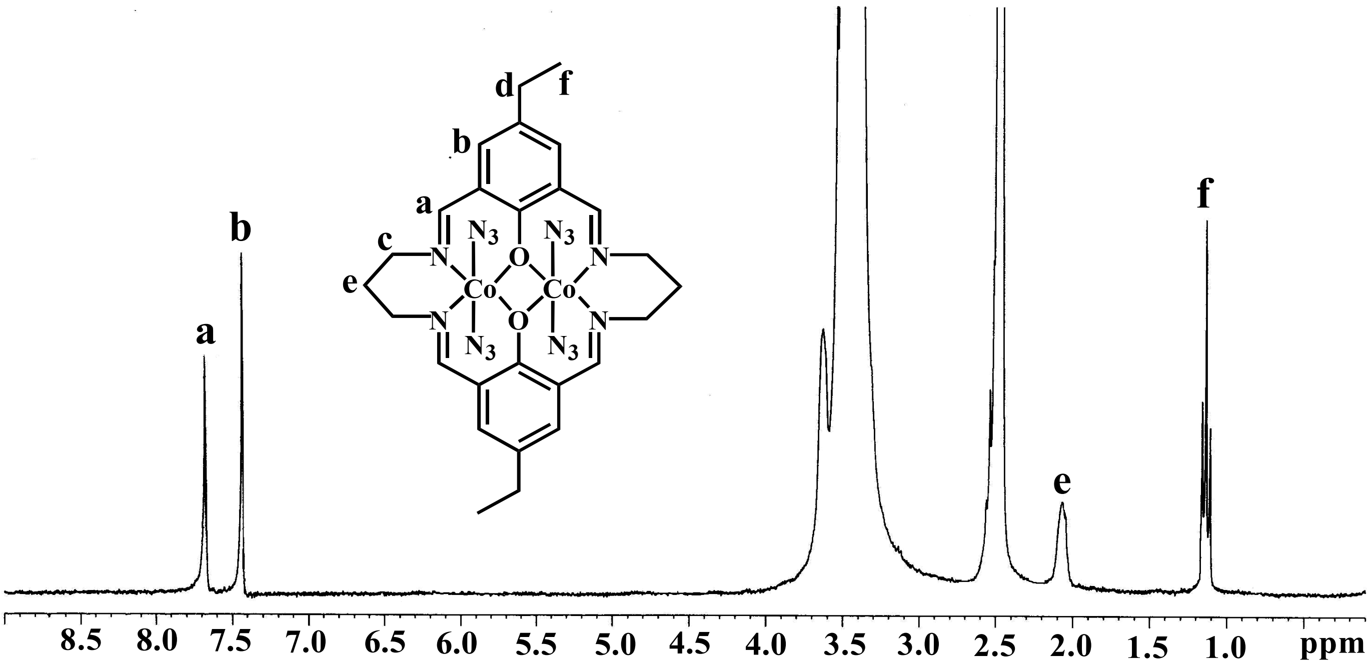


Fig. S2 ^{1}H NMR spectrum of $[\mathrm{Co^{III}Co^{III}L^{Et-pn}(N_3)_4}]\cdot 3.5H_2O$ (**3**; the sample with which spectrum was recorded contains two and half water instead of three and half water of crystallization).

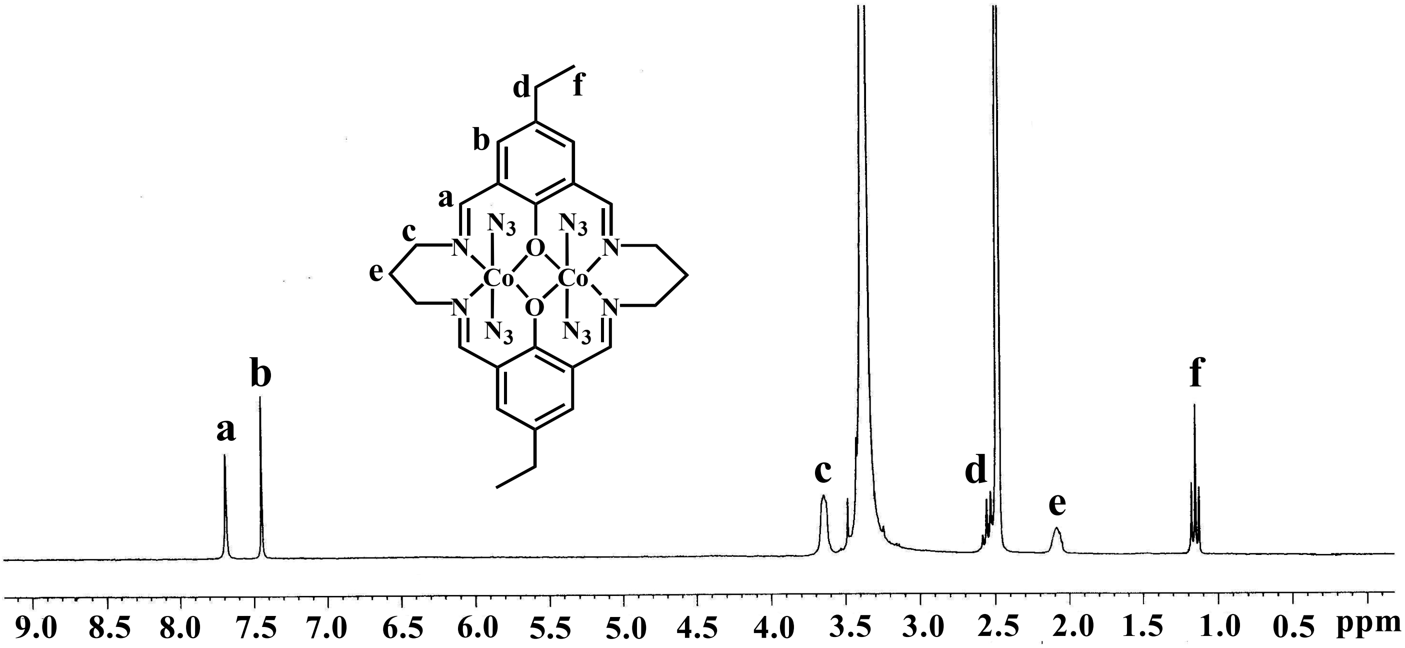


Fig. S3 ^{1}H NMR spectrum of [$\mathrm{Co^{III}Co^{III}L^{Et\text{-}pn}(N_3)_4}$]$\cdot$$CH_3CN$$\cdot$$2.5H_2O$ (**4**; the sample with which spectrum was recorded contains one water instead of one acetonitrile and two and half water of crystallization).

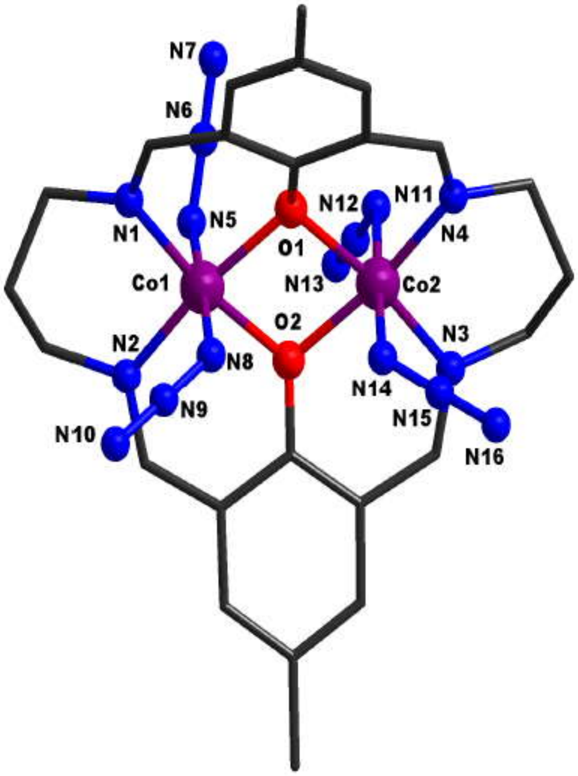


Fig. S4 Crystal structure of $[Co^{III}Co^{III}L^{Me-pn}(N_3)_4]\cdot4H_2O$ (**2**). Hydrogen atoms and water molecules are omitted for clarity. Carbon atoms are shown as wires/sticks.

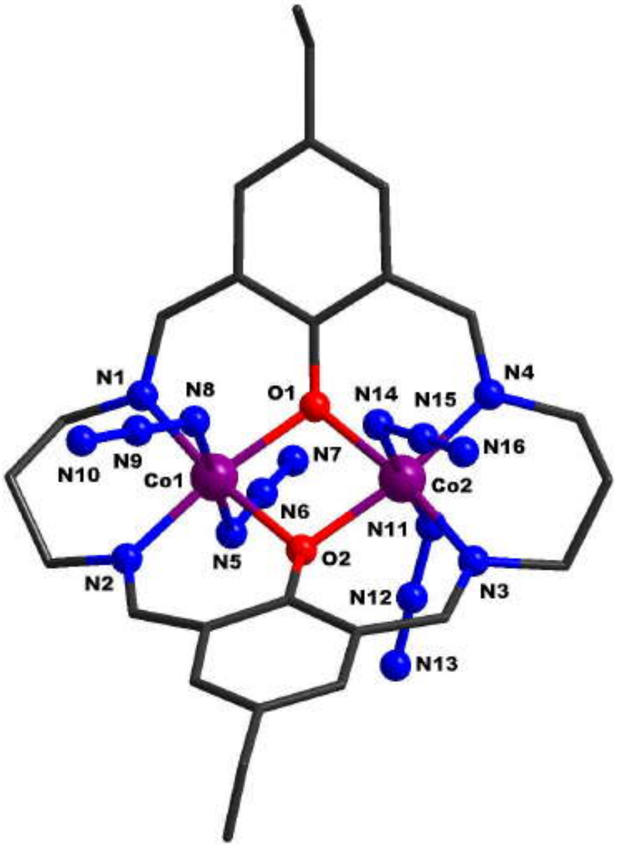
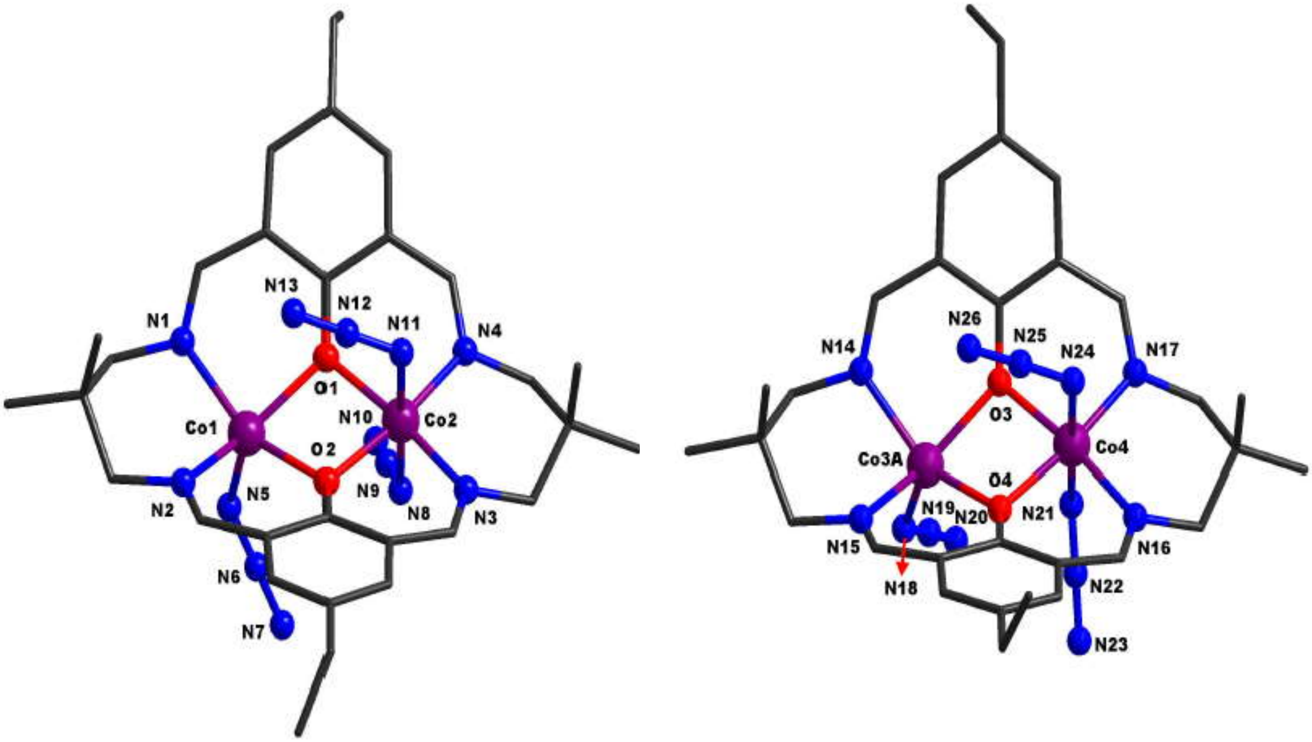


Fig. S5 Crystal structure of $[Co^{III}Co^{III}L^{Et-pn}(N_3)_4]\cdot CH_3CN\cdot 2.5H_2O$ (**4**). Hydrogen atoms, acetonitrile and water molecules are omitted for clarity. Carbon atoms are shown as wires/sticks.



Unit-I

Unit-II

Fig. S6 Crystal structure of $[\mathrm{Co^{III}Co^{II}L^{Et-Me2pn}(N_3)_3}]\cdot\mathrm{H_2O}$ (**6**). Hydrogen atoms and water molecule are omitted for clarity. Carbon atoms are shown as wires/sticks.

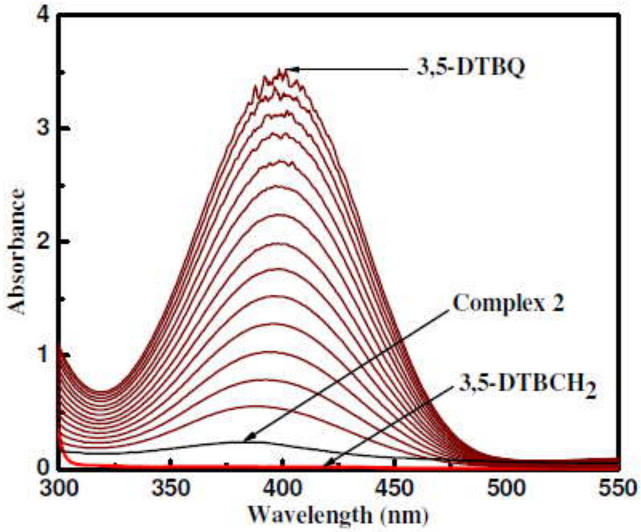


Fig. S7 The spectral profile showing the increase of quinone band at 400 nm after the addition of 100 fold of 3,5-DTBCH$_2$ to a solution containing the complex [Co^{III}Co^{III}L$^{Me–pn}$(N$_3$)$_4$]·4H$_2$O (**2**) (0.25×10^{-4} M) in MeCN. The spectra were recorded after each 5 min.

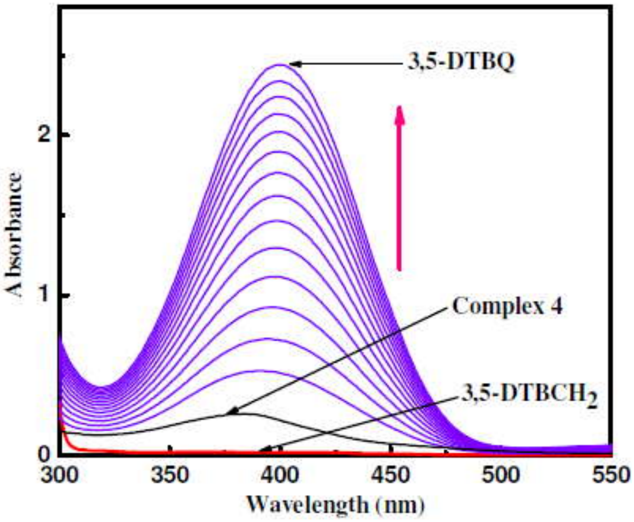


Fig. S8 The spectral profile showing the increase of quinone band at 400 nm after the addition of 100 fold of 3,5-DTBCH$_2$ to a solution containing the complex [Co^{III}Co^{III}L$^{Et–pn}$(N$_3$)$_4$]·CH$_3$CN·2.5H$_2$O (**4**) (0.25×10^{-4} M) in MeCN. The spectra were recorded after each 5 min.

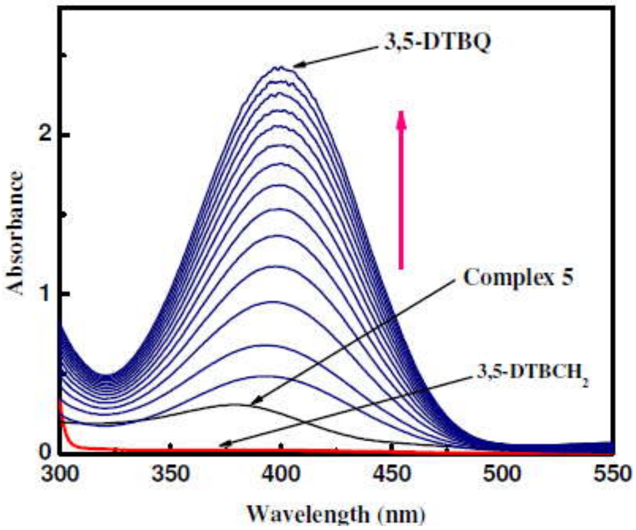


Fig. S9 The spectral profile showing the increase of quinone band at 400 nm after the addition of 100 fold of 3,5-DTBCH$_2$ to a solution containing the complex [Co^{III}Co^{II}L$^{Me-Me2pn}$(N$_3$)$_3$]·2H$_2$O (**5**) (0.25×10^{-4} M) in MeCN. The spectra were recorded after each 5 min.

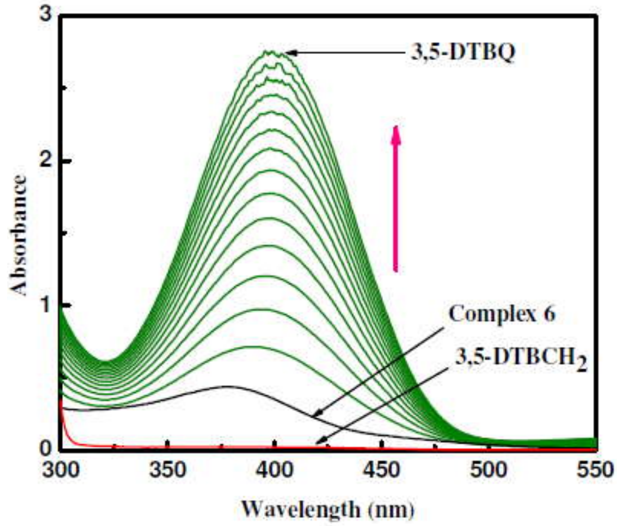


Fig. S10 The spectral profile showing the increase of quinone band at 400 nm after the addition of 100 fold of 3,5-DTBCH$_2$ to a solution containing the complex [Co^{III}Co^{II}L$^{Et-Me2pn}$(N$_3$)$_3$]·H$_2$O (**6**) (0.25×10^{-4} M) in MeCN. The spectra were recorded after each 5 min.

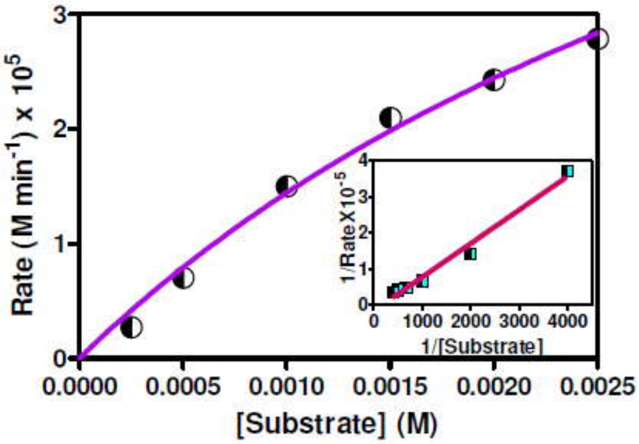


Fig. S11 Initial rates versus substrate concentration for the 3,5-DTBCH$_2$→3,5-DTBQ oxidation reaction catalyzed by complex [Co^{III}Co^{II}L$^{Et-Me2pn}$(N$_3$)$_3$]·H$_2$O (**6**) in acetonitrile. Inset shows Lineweaver-Burk plot. Symbols and solid lines represent the observed and simulated profiles, respectively.

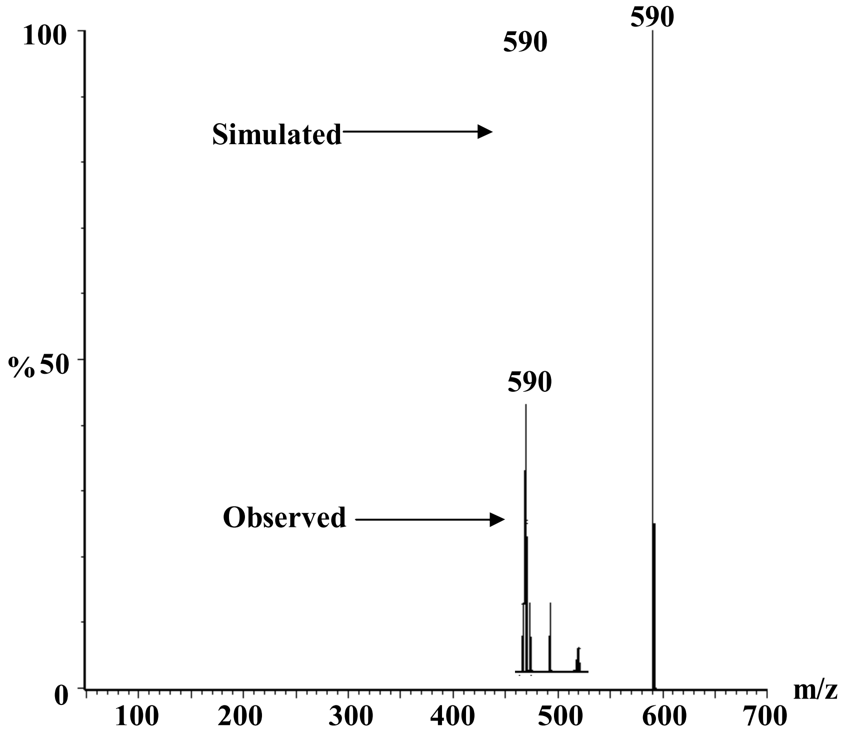


Fig. S12 Electrospray mass spectrum (ESI-MS positive) of [Co^{III}Co^{III}L^{Et-pn}(N$_3$)$_4$]·3.5H$_2$O (**3**) in acetonitrile showing observed and simulated isotopic distribution pattern. m/z values quoted here are for the major peak in the isotope pattern.

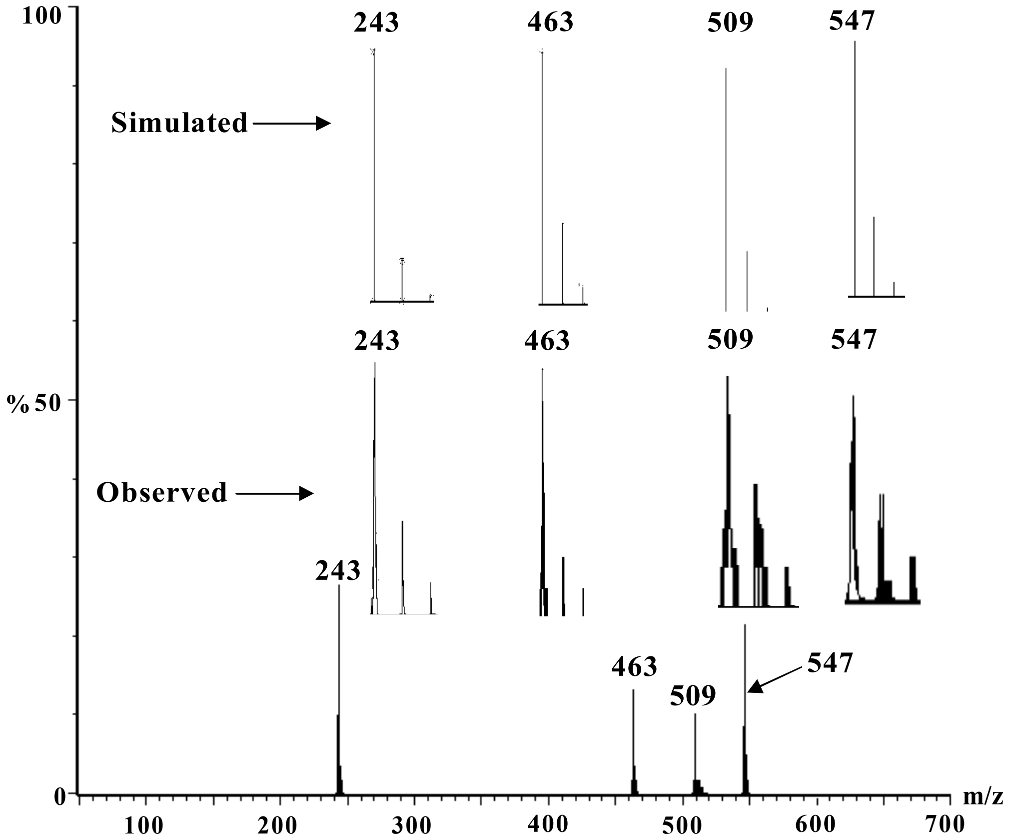


Fig. S13 Electrospray mass spectrum (ESI-MS positive) of a 1:100 mixture of $[Co^{III}Co^{III}L^{Me-pn}(N_3)_4]\cdot 6H_2O$ (**1**) and 3,5-$DTBCH_2$ in acetonitrile, recorded after 5 minutes of mixing. Both the observed and simulated isotopic distribution patterns are shown. m/z values quoted here are for the major peak in the isotope pattern.

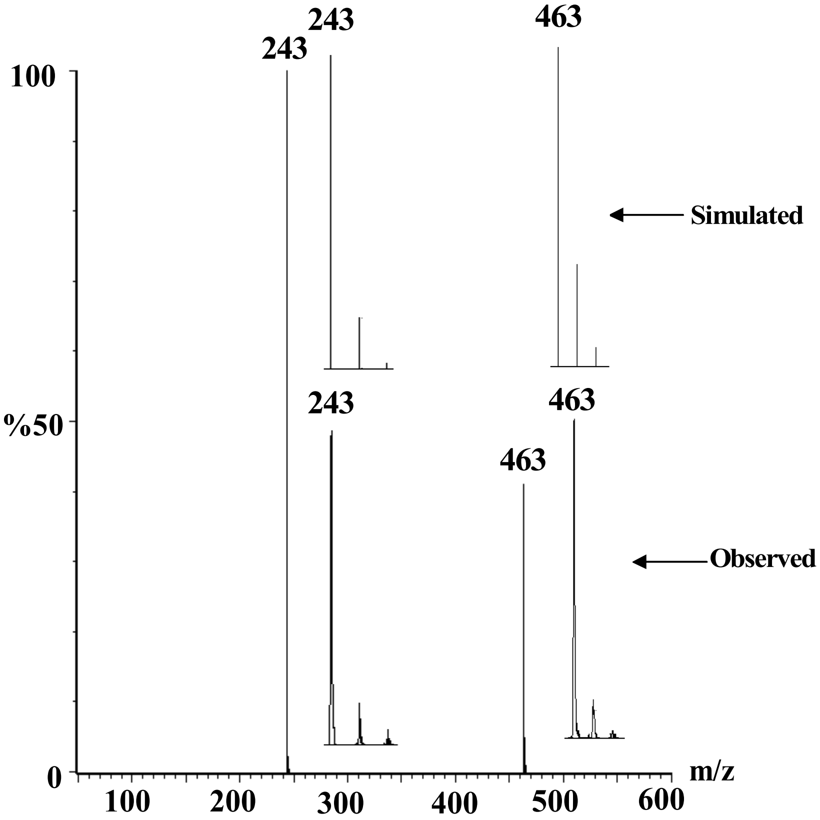


Fig. S14 Electrospray mass spectrum (ESI-MS positive) of a 1:100 mixture of $Co^{III}Co^{III}L^{Et-pn}(N_3)_4]\cdot 3.5H_2O$ (**3**) and 3,5-DTBCH$_2$ in acetonitrile, recorded after 5 minutes of mixing. Both the observed and simulated isotopic distribution patterns are shown. m/z values quoted here are for the major peak in the isotope pattern.

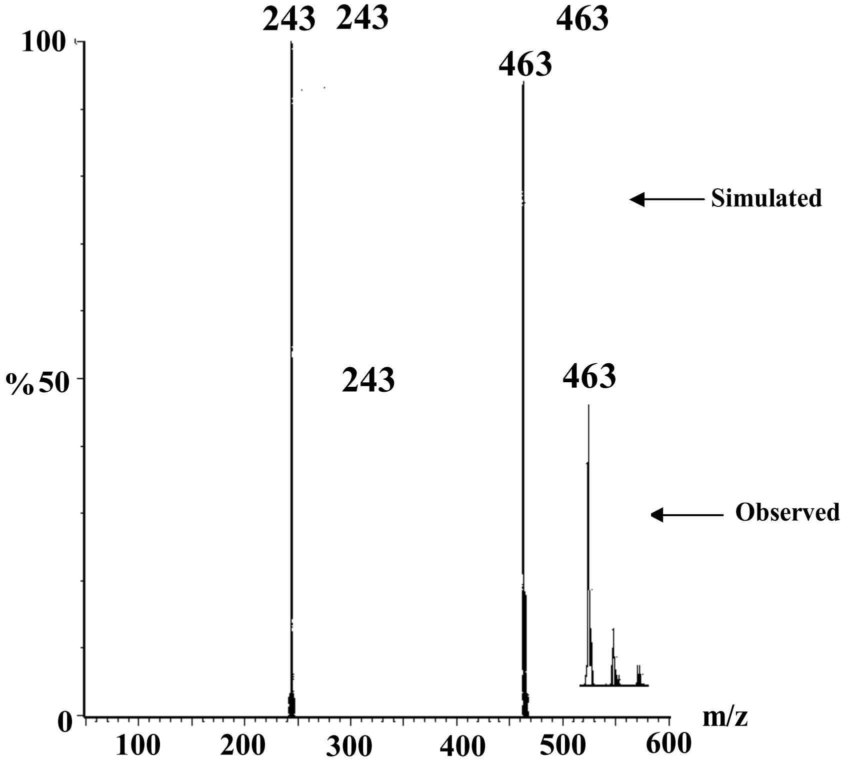


Fig. S15 Electrospray mass spectrum (ESI-MS positive) of a 1:100 mixture of $Co^{III}Co^{III}L^{Et-pn}(N_3)_4]\cdot 3.5H_2O$ (**3**) and 3,5-DTBCH$_2$ in acetonitrile, recorded after 15 minutes of mixing. Both the observed and simulated isotopic distribution patterns are shown. m/z values quoted here are for the major peak in the isotope pattern.

References

S1 L. Mandal, S. Sasmal, H. A. Sparkes, J. A. K. Howard and S. Mohanta, *Inorg. Chim. Acta*, 2014, **412**, 38.

S2 S. Majumder, S. Mondal, P. Lemoine and S. Mohanta, *Dalton Trans.*, 2013, **42**, 4561.