Synthesis, structure and properties of $\{M_4O_4\}$ cubanes containing nickel(II) and cobalt(II)

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Supplementary material

Figure S1. IR spectra of $[Co_4(RR\text{-}1\text{-}H)_4](ClO_4)_4(C_2H_6O)_9$ (Co_41_4) (below) and $[Ni_4(SS\text{-}1\text{-}H)_4](ClO_4)_4(H_2O)_5$ (Ni_41_4) (above) in a KBr pellet.

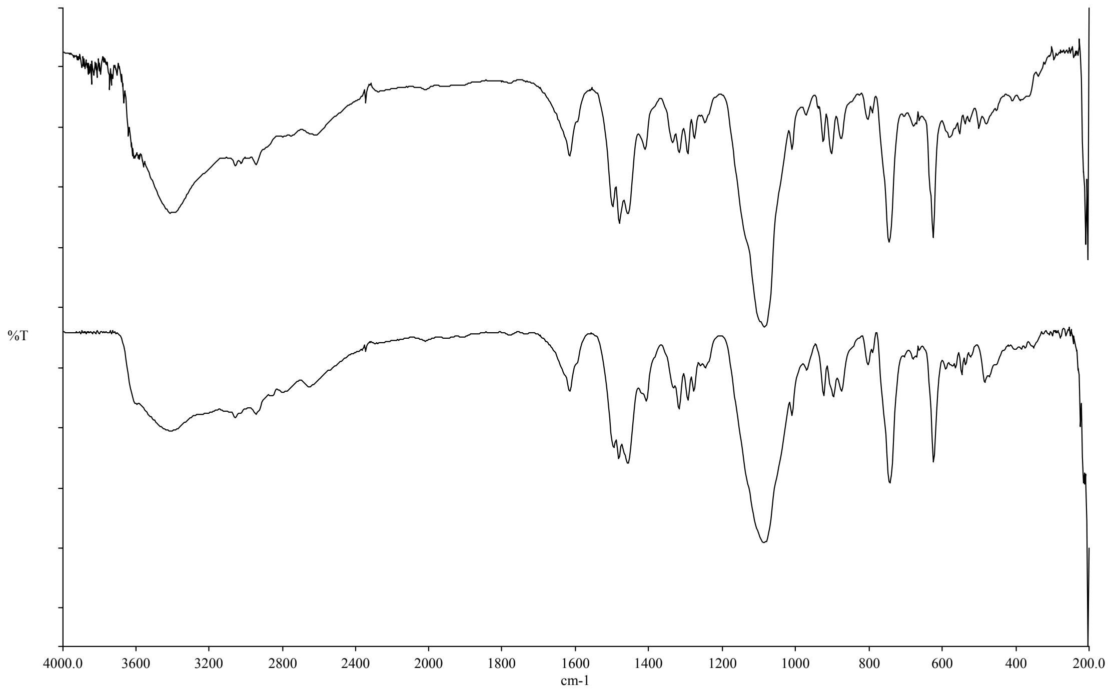

Figure S2. Electrospray mass spectrum of **Co_41_4** in acetonitrile showing the tetrameric species $[Co_4(RR\text{-}\mathbf{1}\text{-}H)_4(\text{-}2H)]^{2+}$.

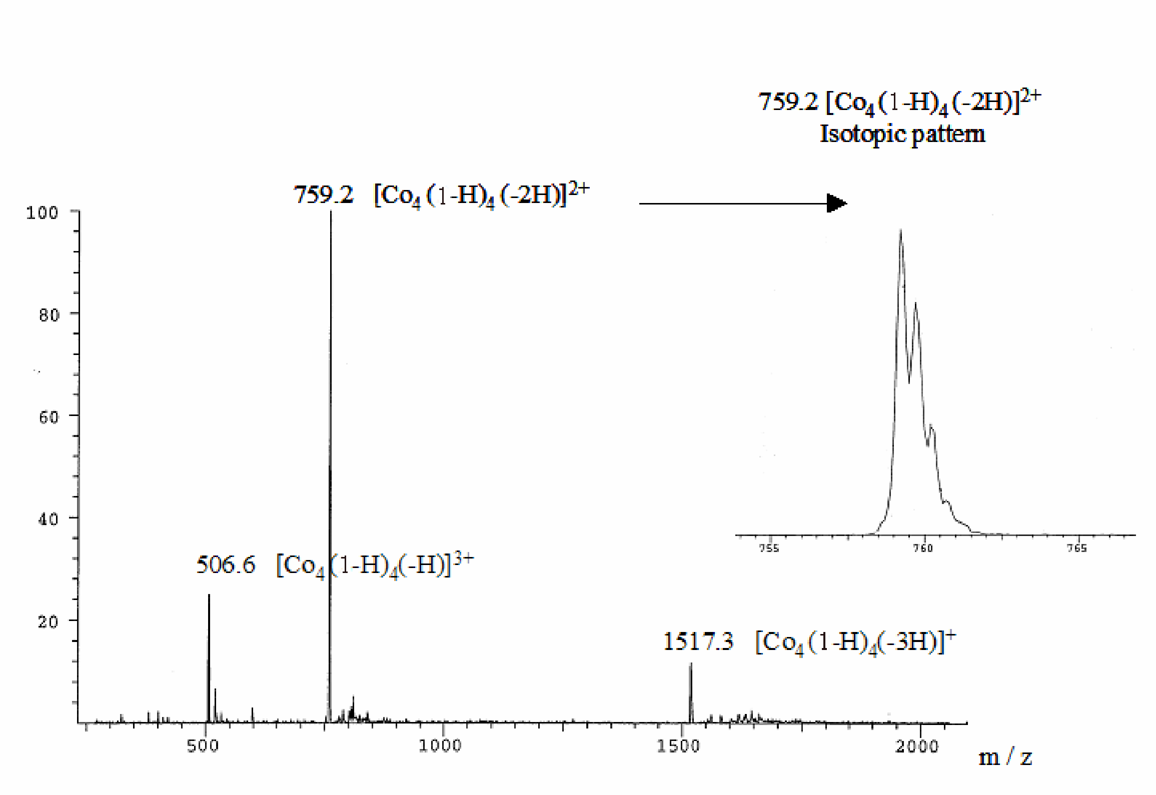

Figure S3. ^{1}H-NMR COSY spectrum of $[Ni_4(\mathit{SS}\text{-}\mathbf{1}\text{-}H)_4]^{4+}$ ($\mathbf{Ni_4 1_4}$) in CD_3CN (T: 21° C) showing eight couplings: 1-8, 8-5, 2-7, 7-6, 3-11, 11-10, 4-12, 12-9. A magnification of the first spectrum shows the couplings 1-8 and 2-7 separately.

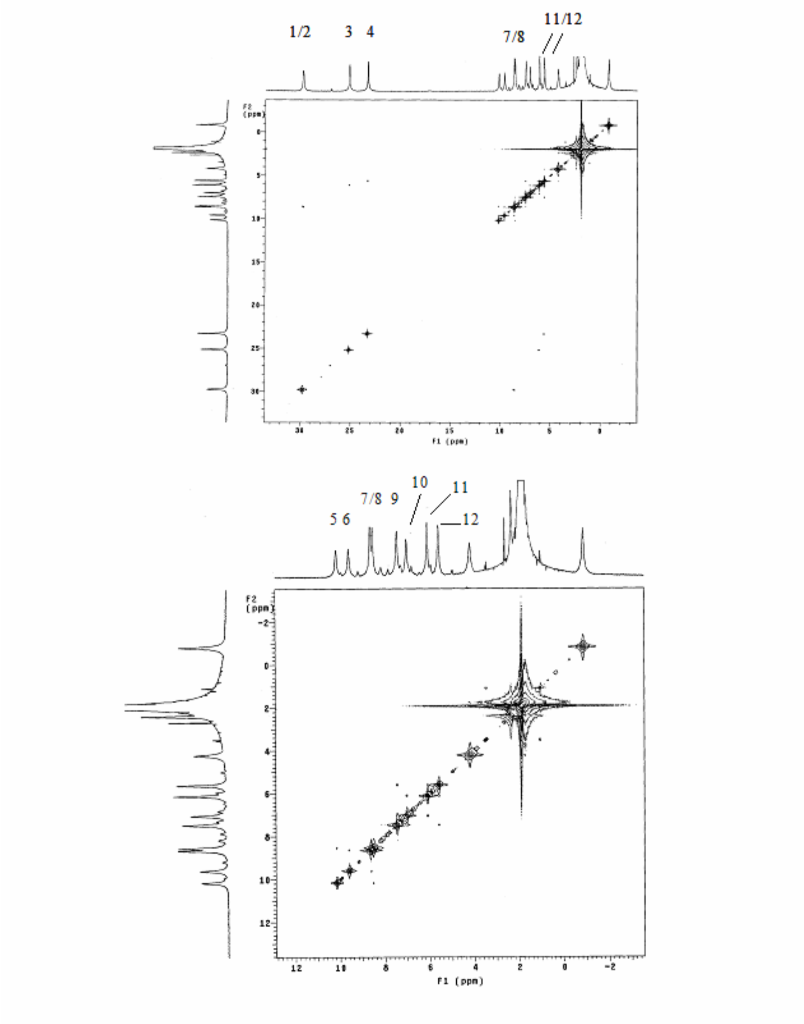

Figure S4. ^{1}H-NMR spectrum of $[Ni_4(\mathit{SS}\text{-}\mathbf{1}\text{-}H)_4]^{4+}$ ($\mathbf{Ni_4 1_4}$) in DMSO-d_6 in the range of -2 to 4.8 ppm. At 21° C only three methyls are observed, while at 50° C a fourth methyl signal appears, which was covered by the water or DMSO signal at 21° C. (* solvent peak, ° H_2O peak, + signals of ethanol, x: signal belonging to a secondary species appearing at 50° C).

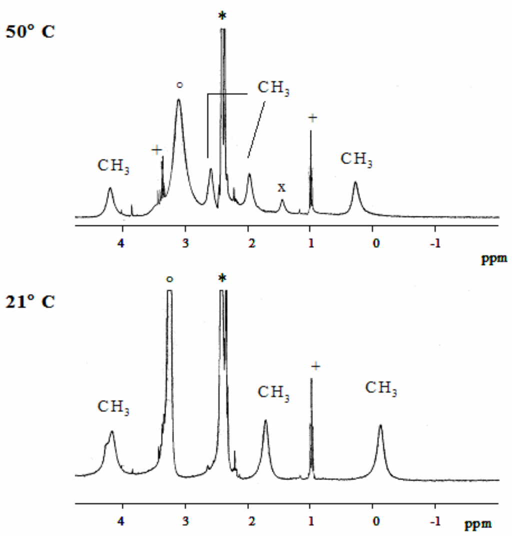

Figure S5. [1]H-NMR COSY spectrum of compound **$Co_4$1$_4$** in CD_3CN showing three cross peaks: 1-3; 4-5 and 5-6 (T: 22° C). A coupling between signal 2 and 3 would allow to attribute each three signals to one benzimidazole unit. We assume that the relaxation times are too short to observe a coupling.

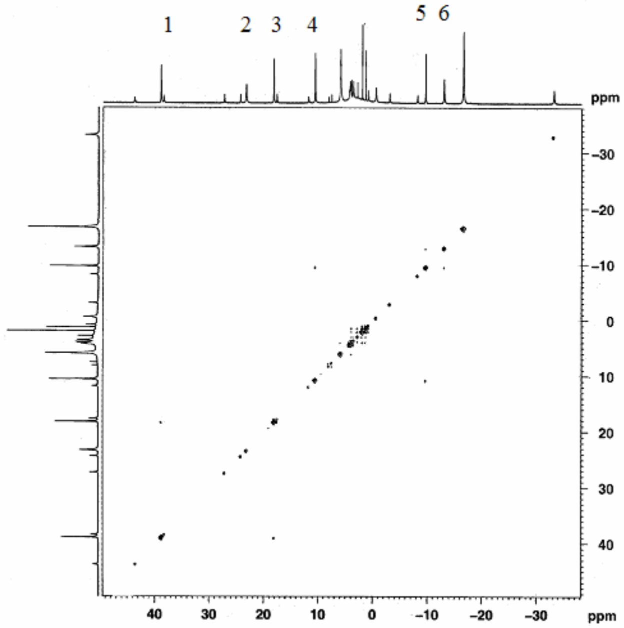

Table S1. Data for cobalt(III) cubanes in the CSD. Dist. : magnitude of the distortion based on the s.d. of the mean Co-Co distance (low < 0.03 Å; high > 0.1 Å). Symmetry : approximate symmetry of the distortion from T_d.

CSD code	Co-Co mean (Å)	s.d. (Å)	Dist.	Symmetry	Ligand coding	Ref.
EYUHIP	2.759	0.078			$Co_4/0s_4/m_6d_3$	1
UMAJUN	2.783	0.086		C_3	$Co_4/0s_4/m_6d_3$	2
VAQLOO	2.728	0.070		S_4-	$Co_4/0s_4/m_4d_4$	3
FIQPUQ	2.877	0.118	high		$Co_4/0s_4/b_4d_2$	4
FIQQAX	2.820	0.104	high		$Co_4/0s_4/b_4d_2$	4
LETYUE	2.820	0.103	high		$Co_4/0s_4/b_4d_2$	5
UBOSIN	2.794	0.111	high	S_4+	$Co_4/0s_4/b_4d_2$	6
WARZEU	2.789	0.097		S_4+	$Co_4/0s_4/b_4d_2$	7
PUDJED	2.799	0.025			$Co_4/0s_4/t_4$	8

Table S2. Data for nickel(II) cubanes in the CSD. Dist. : magnitude of the distortion based on the s.d. of the mean Ni-Ni distance (low < 0.03 Å; high > 0.1 Å). Symmetry : approximate symmetry of the distortion from T_d.

CSD code	Ni-Ni mean (Å)	s.d. (Å)	Dist.	Symmetry	Ligand coding	Ref.
ZIGTOY	3.090	0.032			$Ni_4/0s_4/m_{10}b$	9
BEWKIY	3.086	0.081		C3-	$Ni_4/0s_4/m_3b_3$	10
COLCAH	3.045	0.061		S4-	$Ni_4/0s_4/m_4b_4$	11
ELELIQ	3.081	0.067			$Ni_4/0s_4/t_4$	12
GIVLUS	3.081	0.016	low	S4-	$Ni_4/0s_4/m_4b_4$	13
HAJCAX	3.047	0.140	high	S4+	$Ni_4/0s_4/m_4b_2d_2$	14
IBOGAI	3.050	0.139	high	S4+	$Ni_4/0s_4/m_4b_2d_2$	15
PAGXEA	3.111	0.075		S4-	$Ni_4/0s_4/m_4d_4$	16
TACNIH	3.176	0.012	low	C3+	$Ni_4/0s_4/t_4$	17
TOQDEI	3.074	0.028	low	C3-	$Ni_4/0s_4/m_4b_4$	18
TOQDEI	3.075	0.032			$Ni_4/0s_4/m_4b_4$	18
ZAHROP	3.082	0.023	low	S4-	$Ni_4/0s_4/m_4b_4$	19
ZAXJUD	3.088	0.036		S4-	$Ni_4/0s_4/m_4b_4$	20
AKISOC	3.121	0.023		S4-	$Ni_4/1s_4/m_8$	21
AKISOC	3.133	0.043		S4-	$Ni_4/1s_4/m_8$	21
AKISUI	3.122	0.032		S4-	$Ni_4/1s_4/m_8$	21
BEPBED	3.143	0.035		S4-	$Ni_4/1s_4/m_8$	22
BEPBED	3.124	0.018	low	S4-	$Ni_4/1s_4/m_8$	22
BEPBED	3.140	0.034		S4-	$Ni_4/1s_4/m_8$	21
BEPBED	3.117	0.015	low	S4-	$Ni_4/1s_4/m_8$	21
BEPBON	3.106	0.053		S4-	$Ni_4/1s_4/m_8$	22
BEPBON	3.106	0.042		S4-	$Ni_4/1s_4/m_8$	22
DABNUP	3.178	0.020	low	D2	$Ni_4/1s_4/m_8$	23
DURXIX	3.122	0.054		D2	$Ni_4/1s_4/b_4$	24
EHACOF	3.088	0.079		S4-	$Ni_4/1s2_4/m_4$	25
EHACOF	3.094	0.080		S4-	$Ni_4/1s2_4/m_4$	26
EZIGAV	3.064	0.005	low	S4+	$Ni_4/2s_4/m_4$	27
HMZHNI	3.107	0.076		S4-	$Ni_4/1s2_4/m_4$	28
MAWZUF	3.133	0.122	high	C2	$Ni_4/2s_4/m_2d$	29
MSALEN	3.072	0.015	low	S4-	$Ni_4/0s_4/m_4b_4$	30
MUZLOI	3.133	0.070			$Ni_4/0s_2,2s22_2/m_4$	31
MUZLOI	3.141	0.074			$Ni_4/0s_2,2s22_2/m_4$	31
HUBZAF	3.103	0.131	high	S4+	$Ni_4/0s,1s,2s22_2/m_3d_2$	32
HUBZAF	3.103	0.130	high	S4+	$Ni_4/0s,1s,2s22_2/m_3d_2$	32
UMUFUD	3.094	0.126	high	S4-	$Ni_4/1s_4/d_4$	33
WEBSEB	3.155	0.102	high	S4+	Ni_4/bi-$2s_4$/*	34
YAQYAR	3.184	0.072		D2	$Ni_4/2s_4/m_4$	35
DARPES	3.093	0.084		S4-	$Ni_4/1s2_4/m_4$	36
DARPES	3.094	0.088		S4-	$Ni_4/1s2_4/m_4$	36
EHACOF	3.095	0.086		S4-	$Ni_4/1s2_4/m_4$	36

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