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COORDINATION COMPOUNDS

Synthesis and Structure of Trinuclear Pyrazolate-Bridged Acetates $M_3(\mu\text{-dmpz})_4(Hdmpz)_2(OOCMe)_2$ (M = Zn or Co; Hdmpz = 3,5-Dimethylpyrazole)

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Abstract—We discovered that reactions of hydrous cobalt and zinc acetates with 3,5-dimethylpyrazole (Hdmpz) in boiling xylene or toluene or upon the thermolysis of solid precursors (150°C) yield trinuclear pyrazolate-bridged complexes $M_3(\mu\text{-dmpz})_4(Hdmpz)_2(OOCMe)_2$ (M = Zn or Co). Depending on the crystallization conditions, these complexes contain various solvating molecules (benzene, toluene, or Hdmpz), which influences the character of intramolecular and intermolecular hydrogen bonding, as shown by X-ray crystallography.

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Transition-metal carboxylates (acetates) are conventionally used in advanced coordination chemistry as precursors for complexes with coordinated organic ligands. In many cases, the formation of new compounds in such reactions is accompanied by proton transfer from an organic molecule with the appearance of the corresponding anion and recovery of carboxylic acid. Depending on the reaction parameters, deprotonation of pyrazole or its analogues in the presence of transition-metal carboxylates (acetates) yields di-, tri-, or polynuclear complexes and pyrazolate-bridged polymers [1–6].

For example, possible intermediates of the reactions yielding acetate-pyrazolate- and pyrazolate-bridged polymers $[Zn(\mu\text{-OOCMe})(\mu\text{-pz})]_n$ and $[Zn(\mu\text{-pz})_2]_n$ were recovered as a result of a comprehensive study of the reaction between hydrous zinc acetate and pyrazole in alcohol or water at room temperature [1].

It was found, however, that the reactions of dinuclear pivalates $M_2(\mu\text{-OOCBu}^t)_4(NEt_3)_2$ (M = Zn or Co) with 3,5-dimethylpyrazole (Hdmpz) at room temperature result in pyrazole deprotonation and the formation of pyrazolate-bridged dimers $M_2(\mu\text{-dmpz})_2(Hdmpz)_2(OOCBu^t)_2$ [7–10].

Continuing on our studies of the specifics of 3,5-dimethylpyrazole deprotonation as a function of the nature of the transition metal and carboxylate anion, here we discuss the structures of products of the reaction of hydrous cobalt and zinc acetates with 3,5-dimethylpyrazole in a boiling organic solvent (toluene or xylene) and thermolysis at 150°C. We also consider the influence of the nature of the transition metal and solvating molecules on intramolecular and intermolecular hydrogen bonding in the complexes synthesized.

EXPERIMENTAL

All operations in the synthesis and recovery of complexes were carried out in a pure argon atmosphere using absolute solvents.

IR spectra were recorded as KBr discs on a Specord M-80 spectrophotometer over the frequency range 392–4000 cm^{-1}.

X-ray crystallography experiments were performed using a routine procedure on a Bruker Smart Apex II automated diffractometer equipped with a CCD detector (λMo, graphite monochromator, ω scans). Structures were solved using the SHELXTL PLUS program package (a PC version). Structure refinement was performed using the SHELXTL-97 program package [11, 12].

Crystal data and the details of structure refinement are listed in Table 1. Atomic coordinates and selected geometric parameters of the complexes are in Tables 2–11.

Syntheses

$Co_3(\mu\text{-dmpz})_4(Hdmpz)_2(OOCMe)_2$ (1). To 3,5-dimethylpyrazole (0.044 g, 0.46 mmol) in xylene (20 mL), hydrous cobalt acetate (0.1 g, 0.23 mmol) was added. This suspension was heated for 30 min with stirring at 145°C until complete dissolution. The resulting violet solution was reduced in volume to 10 mL and allowed at stand for 24 h at –5°C. Violet crystals were separated

Table 1. Crystallographic parameters and details of structure refinement for **1**–**5**

	1	**2** (**1** × 0.5C_6H_5Me)	**3** (**1** × 0.5C_6H_6)	**4** × C_6H_6	**5** (**1** × Hdmpz)
Bulk formula	$C_{34}H_{50}Co_3N_{12}O_4$	$C_{37.5}H_{53.5}Co_3N_{12}O_4$	$C_{37}H_{53}Co_3N_{12}O_4$	$C_{40}H_{56}N_{12}O_4Zn_3$	$C_{39}H_{58}Co_3N_{14}O_4$
FW	867.65	913.21	906.70	965.08	963.78
T, K	120(2)	120(2)	120(2)	120(2)	120(2)
Color	Violet	Violet	Violet	Water color	Violet
Crystals system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	*P*2(1)/*c*	*P*2(1)/*c*	*P*2(1)/*c*	*P*-1	*P*2(1)/*c*
Unit cell parameters					
a, Å	13.3691(16)	13.2196(6)	13.285(7)	8.381(2)	18.2553(16)
b, Å	14.6453(18)	17.1872(7)	17.389(10)	16.389(4)	14.3583(13)
c, Å	21.143(3)	19.3268(8)	19.794(11)	19.272(5)	19.3896(19)
α, deg	90	90	90	113.144(4)	90
β, deg	93.162(2)	97.9150(10)	96.772(10)	101.980(4)	112.018(2)
γ, deg	90	90	90	90.897(4)	90
V, Å^3	4133.4(9)	4349.4(3)	4541(4)	2367.2(11)	4711.6(8)
Z	4	4	4	2	4
ρ_{calc}, mg/m^3	1.394	1.395	1.326	1.354	1.359
M, mm^{-1}	1.240	1.183	1.132	1.558	1.097
F(000)	1804	1902	1888	1004	2012
Crystal size, mm	0.14 × 0.12 × 0.10	0.14 × 0.12 × 0.10	0.14 × 0.12 × 0.10	0.12 × 0.10 × 0.08	0.12 × 0.10 × 0.08
θ scan range, deg	1.69–25.00	2.37–29.00	1.94–27.00	2.13–25.00	1.82–25.00
Reflection index ranges	$-15 \le h \le 15$, $-17 \le k \le 17$, $-20 \le l \le 25$	$-18 \le h \le 18$, $-23 \le k \le 20$, $-26 \le l \le 26$	$-16 \le h \le 16$, $-22 \le k \le 22$, $-25 \le l \le 25$	$-9 \le h \le 9$, $-19 \le k \le 19$, $-22 \le l \le 22$	$-21 \le h \le 11$, $-16 \le k \le 16$, $-5 \le l \le 23$
Reflections	24698	32532	41900	15307	11253
Independent reflections	7171 [*R*(int) = 0.1010]	11404 [*R*(int) = 0.0601]	9700 [*R*(int) = 0.1533]	7676 [*R*(int) = 0.1186]	7182 [*R*(int) = 0.0640]
GOOF	0.898	0.993	0.871	0.977	0.818
R ($I > 2\sigma(I)$)	*R*1 = 0.0476, *wR*2 = 0.0663	*R*1 = 0.0312, *wR*2 = 0.0578	*R*1 = 0.0484, *wR*2 = 0.0840	*R*1 = 0.0793, *wR*2 = 0.0820	*R*1 = 0.0447, *wR*2 = 0.0638
R (on all reflections)	*R*1 = 0.1236, *wR*2 = 0.0778	*R*1 = 0.0477, *wR*2 = 0.0604	*R*1 = 0.1367, *wR*2 = 0.0996	*R*1 = 0.1954, *wR*2 = 0.1069	*R*1 = 0.1074, *wR*2 = 0.0743
Electron density peaks (min/max), e Å^{-3}	1.045, –0.378	0.492, –0.320	1.028, –0.668	0.596, –0.860	0.406, –0.315

Table 2. Coordinates of atoms ($\times 10^4$) and their equivalent isotropic factors ($Å^2 \times 10^3$) for complex **1**

Atom	x	y	z	U_{eq}
Co(1)	–8732(1)	7915(1)	1351(1)	47(1)
Co(2)	–6169(1)	7463(1)	1000(1)	54(1)
Co(3)	–11208(1)	8022(1)	1933(1)	55(1)
O(1)	–5596(3)	6659(3)	1662(2)	96(1)
O(2)	–4627(3)	7764(3)	1826(2)	132(2)
O(3)	–11678(3)	6770(2)	1995(2)	85(1)
O(4)	–12819(3)	7016(3)	1298(3)	165(2)
N(1)	–8287(3)	6803(2)	911(2)	55(1)
N(2)	–7323(3)	6672(2)	731(2)	55(1)
N(3)	–7682(2)	8861(2)	1281(2)	46(1)
N(4)	–6715(2)	8709(2)	1108(2)	48(1)
N(5)	–9961(2)	8332(2)	852(2)	52(1)
N(6)	–10865(3)	8514(2)	1110(2)	52(1)
N(7)	–9014(3)	7888(2)	2260(2)	56(1)
N(8)	–9954(3)	7951(2)	2496(2)	56(1)
N(9)	–5228(3)	7527(2)	286(2)	54(1)
N(10)	–4262(3)	7265(2)	328(2)	69(1)
N(11)	–12139(3)	8932(3)	2310(2)	62(1)
N(12)	–13080(3)	8719(3)	2464(2)	72(1)
C(1)	–8846(4)	6096(3)	690(3)	71(2)
C(2)	–9937(3)	6044(3)	800(3)	104(2)
C(3)	–8261(4)	5513(3)	366(3)	89(2)
C(4)	–7302(4)	5874(3)	396(3)	71(2)
C(5)	–6376(4)	5499(4)	135(3)	106(2)
C(6)	–7798(3)	9754(3)	1387(2)	48(1)
C(7)	–8747(3)	10142(3)	1607(2)	66(1)
C(8)	–6907(4)	10195(3)	1280(2)	62(1)
C(9)	–6256(3)	9529(3)	1107(2)	52(1)
C(10)	–5186(3)	9633(3)	952(2)	85(2)
C(11)	–9988(4)	8627(3)	249(3)	57(1)
C(12)	–9128(4)	8524(3)	–155(2)	81(2)
C(13)	–10930(4)	9003(3)	106(3)	69(2)
C(14)	–11438(4)	8929(3)	648(3)	65(1)
C(15)	–12484(3)	9229(3)	750(3)	99(2)
C(16)	–8354(4)	7868(3)	2756(3)	73(2)
C(17)	–7242(3)	7815(4)	2676(2)	115(2)
C(18)	–8848(4)	7901(4)	3306(3)	85(2)
C(19)	–9869(4)	7949(3)	3133(3)	69(1)
C(20)	–10735(4)	7995(4)	3526(2)	102(2)
C(21)	–11960(4)	9741(4)	2579(3)	74(2)
C(22)	–10991(4)	10216(3)	2519(3)	122(3)
C(23)	–12774(5)	10023(4)	2890(3)	88(2)
C(24)	–13491(4)	9367(4)	2799(3)	80(2)
C(25)	–14542(4)	9279(4)	3027(3)	120(2)
C(26)	–5429(4)	7735(3)	–309(3)	66(1)
C(27)	–6453(4)	8072(4)	–542(2)	101(2)
C(28)	–4577(4)	7628(4)	–657(3)	82(2)
C(29)	–3846(4)	7321(3)	–236(3)	77(2)
C(30)	–2770(4)	7097(4)	–329(3)	116(2)
C(31)	–4947(5)	7035(5)	1995(3)	96(1)
C(32)	–4533(4)	6573(4)	2583(2)	109(2)
C(33)	–12352(5)	6474(5)	1636(4)	100(2)
C(34)	–12542(4)	5494(3)	1634(3)	100(2)

Table 3. Bond lengths (*d*) and bond angles (ω) for complex **1**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Co(1)–N(7)	1.980(4)	N(11)–N(12)	1.353(4)	Co(1)–N(5)	1.999(3)	C(1)–C(2)	1.492(6)
Co(1)–N(1)	1.984(3)	C(1)–C(3)	1.368(6)	Co(2)–N(4)	1.984(3)	C(4)–C(5)	1.488(6)
Co(2)–O(1)	1.953(4)	C(3)–C(4)	1.385(6)	Co(2)–N(9)	2.021(3)	C(6)–C(7)	1.488(5)
Co(2)–N(2)	1.986(4)	C(6)–C(8)	1.385(5)	Co(3)–N(6)	1.960(4)	C(9)–C(10)	1.494(6)
Co(3)–O(3)	1.944(3)	C(8)–C(9)	1.371(6)	Co(3)–N(11)	2.018(4)	C(11)–C(12)	1.476(6)
Co(3)–N(8)	2.005(4)	C(11)–C(13)	1.392(6)	O(2)–C(31)	1.211(6)	C(14)–C(15)	1.493(6)
O(1)–C(31)	1.218(6)	C(13)–C(14)	1.369(6)	O(4)–C(33)	1.215(7)	C(16)–C(17)	1.507(6)
O(3)–C(33)	1.226(7)	C(16)–C(18)	1.371(6)	N(1)–N(2)	1.377(4)	C(19)–C(20)	1.462(6)
N(1)–C(1)	1.344(5)	C(18)–C(19)	1.396(6)	N(3)–C(6)	1.337(5)	C(21)–C(22)	1.481(6)
N(2)–C(4)	1.369(5)	C(21)–C(23)	1.365(6)	N(4)–C(9)	1.349(5)	C(23)–H(23A)	0.9300
N(3)–N(4)	1.381(4)	C(23)–C(24)	1.363(6)	N(5)–N(6)	1.379(4)	C(26)–C(28)	1.397(6)
N(5)–C(11)	1.345(5)	C(24)–C(25)	1.516(6)	N(7)–C(16)	1.332(5)	C(28)–C(29)	1.361(7)
N(6)–C(14)	1.351(5)	C(26)–C(27)	1.513(6)	N(8)–C(19)	1.346(5)	C(31)–C(32)	1.496(7)
N(7)–N(8)	1.381(4)	C(29)–C(30)	1.499(7)	N(9)–N(10)	1.344(4)		
N(9)–C(26)	1.308(5)	C(33)–C(34)	1.458(7)	N(11)–C(21)	1.331(5)		
N(10)–C(29)	1.345(6)	Co(1)–N(3)	1.984(3)	N(12)–C(24)	1.322(5)		
Angle	**ω, deg**	**Angle**	**ω, deg**	**Angle**	**ω, deg**	**Angle**	**ω, deg**
N(7)Co(1)N(3)	105.03(14)	N(10)N(9)Co(2)	124.9(3)	C(33)O(3)Co(3)	121.4(5)	C(14)C(13)C(11)	105.7(5)
N(3)Co(1)N(1)	107.86(15)	C(21)N(11)N(12)	104.4(4)	C(1)N(1)Co(1)	128.2(3)	N(6)C(14)C(15)	121.7(5)
N(7)Co(1)N(1)	121.14(15)	N(12)N(11)Co(3)	123.1(3)	C(4)N(2)N(1)	107.9(4)	N(7)C(16)C(18)	109.8(5)
N(7)Co(1)N(5)	108.93(16)	N(1)C(1)C(3)	109.4(4)	N(1)N(2)Co(2)	124.4(3)	C(18)C(16)C(17)	128.4(5)
N(3)Co(1)N(5)	108.15(14)	C(3)C(1)C(2)	129.5(5)	C(6)N(3)Co(1)	125.6(3)	N(8)C(19)C(18)	106.8(4)
O(1)Co(2)N(4)	127.20(15)	N(2)C(4)C(3)	107.8(4)	C(9)N(4)N(3)	106.9(3)	C(18)C(19)C(20)	130.3(5)
N(4)Co(2)N(2)	106.52(15)	C(3)C(4)C(5)	128.9(5)	N(3)N(4)Co(2)	122.3(3)	N(11)C(21)C(22)	121.2(5)
N(4)Co(2)N(9)	106.94(14)	N(3)C(6)C(7)	122.3(4)	C(11)N(5)Co(1)	125.3(3)	C(23)C(21)C(22)	128.6(5)
O(3)Co(3)N(6)	119.92(15)	C(9)C(8)C(6)	106.0(4)	C(14)N(6)N(5)	106.0(4)	N(12)C(24)C(23)	105.7(5)
N(6)Co(3)N(8)	108.53(15)	N(4)C(9)C(10)	122.2(4)	N(5)N(6)Co(3)	122.2(3)	C(23)C(24)C(25)	132.3(6)
N(6)Co(3)N(11)	106.73(15)	N(5)C(11)C(13)	108.0(4)	C(16)N(7)Co(1)	127.7(3)	N(9)C(26)C(27)	121.6(5)
C(31)O(1)Co(2)	112.3(4)	C(13)C(11)C(12)	129.7(5)	C(19)N(8)N(7)	109.5(4)	C(29)C(28)C(26)	105.6(5)
C(1)N(1)N(2)	108.0(4)	N(6)C(14)C(13)	110.7(4)	N(7)N(8)Co(3)	122.5(3)	N(10)C(29)C(30)	123.4(6)
N(2)N(1)Co(1)	123.6(3)	C(13)C(14)C(15)	127.5(5)	C(26)N(9)Co(2)	128.8(3)	O(2)C(31)O(1)	118.7(7)
C(4)N(2)Co(2)	127.5(3)	N(7)C(16)C(17)	121.9(5)	N(9)N(10)C(29)	111.5(4)	O(1)C(31)C(32)	119.6(6)
C(6)N(3)N(4)	108.7(3)	C(16)C(18)C(19)	106.8(5)	C(21)N(11)Co(3)	131.1(3)	O(4)C(33)C(34)	123.9(7)
N(4)N(3)Co(1)	125.8(3)	N(8)C(19)C(20)	122.9(5)	C(24)N(12)N(11)	112.6(4)	C(24)C(23)C(21)	107.0(5)
C(9)N(4)Co(2)	130.4(3)	N(11)C(21)C(23)	110.2(5)	N(1)C(1)C(2)	121.0(4)	N(12)C(24)C(25)	121.9(6)
C(11)N(5)N(6)	109.6(4)	N(1)Co(1)N(5)	105.23(14)	C(1)C(3)C(4)	106.9(4)	N(9)C(26)C(28)	110.4(5)
N(6)N(5)Co(1)	124.2(3)	O(1)Co(2)N(2)	96.98(15)	N(2)C(4)C(5)	123.3(5)	C(28)C(26)C(27)	127.9(5)
C(14)N(6)Co(3)	130.9(3)	O(1)Co(2)N(9)	109.13(16)	N(3)C(6)C(8)	108.7(4)	N(10)C(29)C(28)	106.4(5)
C(16)N(7)N(8)	107.1(4)	N(2)Co(2)N(9)	108.60(15)	C(8)C(6)C(7)	128.9(5)	C(28)C(29)C(30)	130.2(6)
N(8)N(7)Co(1)	125.1(3)	O(3)Co(3)N(8)	99.98(15)	N(4)C(9)C(8)	109.7(4)	O(2)C(31)C(32)	121.6(6)
C(19)N(8)Co(3)	128.0(3)	O(3)Co(3)N(11)	112.77(15)	C(8)C(9)C(10)	128.1(4)	O(4)C(33)O(3)	117.9(7)
C(26)N(9)N(10)	106.0(4)	N(8)Co(3)N(11)	108.25(16)	N(5)C(11)C(12)	122.2(4)	O(3)C(33)C(34)	118.2(7)

Table 4. Coordinates of atoms ($\times 10^4$) and their equivalent isotropic factors ($Å^2 \times 10^3$) for $\mathbf{1} \times 0.5C_6H_5Me$ (**2**)

Atom	x	y	z	U_{eq}
Co(1)	3904(1)	8131(1)	1766(1)	15(1)
Co(2)	6408(1)	7966(1)	1228(1)	16(1)
Co(3)	1359(1)	7846(1)	2244(1)	16(1)
O(1)	6841(1)	6883(1)	1197(1)	23(1)
O(2)	8075(1)	7245(1)	2013(1)	31(1)
O(3)	289(1)	7508(1)	1532(1)	25(1)
O(4)	–684(1)	6931(1)	664(1)	24(1)
N(1)	4139(1)	8002(1)	777(1)	16(1)
N(2)	5088(1)	7938(1)	565(1)	18(1)
N(3)	5197(1)	8501(1)	2322(1)	17(1)
N(4)	6128(1)	8549(1)	2075(1)	17(1)
N(5)	3414(1)	7191(1)	2220(1)	17(1)
N(6)	2536(1)	7149(1)	2526(1)	17(1)
N(7)	2855(1)	8970(1)	1784(1)	17(1)
N(8)	1878(1)	8852(1)	1939(1)	16(1)
N(9)	7391(1)	8618(1)	753(1)	17(1)
N(10)	8321(1)	8380(1)	610(1)	18(1)
N(11)	538(1)	7997(1)	3041(1)	18(1)
N(12)	–401(1)	7671(1)	3040(1)	20(1)
C(1)	3434(1)	7942(1)	208(1)	20(1)
C(2)	2312(1)	7980(1)	267(1)	31(1)
C(3)	3913(1)	7841(1)	–381(1)	22(1)
C(4)	4953(1)	7837(1)	–133(1)	19(1)
C(5)	5829(1)	7716(1)	–536(1)	28(1)
C(6)	5278(1)	8876(1)	2936(1)	20(1)
C(7)	4387(1)	8940(1)	3339(1)	27(1)
C(8)	6257(1)	9170(1)	3098(1)	22(1)
C(9)	6767(1)	8955(1)	2546(1)	19(1)
C(10)	7844(1)	9135(1)	2440(1)	23(1)
C(11)	3974(1)	6551(1)	2402(1)	21(1)
C(12)	4994(1)	6432(1)	2165(1)	31(1)
C(13)	3454(1)	6083(1)	2822(1)	23(1)
C(14)	2561(1)	6477(1)	2888(1)	19(1)
C(15)	1703(1)	6249(1)	3283(1)	27(1)
C(16)	2929(1)	9712(1)	1588(1)	20(1)
C(17)	3908(1)	10020(1)	1380(1)	27(1)
C(18)	2002(1)	10088(1)	1605(1)	23(1)
C(19)	1364(1)	9528(1)	1824(1)	20(1)
C(20)	271(1)	9599(1)	1944(1)	29(1)
C(21)	7264(1)	9337(1)	500(1)	18(1)
C(22)	6298(1)	9775(1)	550(1)	24(1)
C(23)	8119(1)	9563(1)	196(1)	21(1)
C(24)	8777(1)	8940(1)	277(1)	20(1)
C(25)	9815(1)	8825(1)	69(1)	28(1)
C(26)	774(1)	8332(1)	3667(1)	22(1)
C(27)	1773(1)	8744(1)	3854(1)	29(1)
C(28)	–21(1)	8224(1)	4061(1)	25(1)
C(29)	–760(1)	7810(1)	3649(1)	22(1)
C(30)	–1799(1)	7540(1)	3772(1)	32(1)
C(31)	7636(1)	6736(1)	1634(1)	21(1)
C(32)	8006(2)	5908(1)	1661(1)	36(1)
C(33)	73(1)	6931(1)	1115(1)	21(1)
C(34)	786(2)	6240(1)	1187(1)	38(1)
C(35)	5169(2)	5709(2)	307(1)	54(1)
C(36)	5959(2)	5339(2)	72(1)	55(1)
C(37)	5816(2)	4607(2)	–244(1)	52(1)
C(38)	6569(3)	4243(3)	–508(2)	43(1)

Table 5. Bond lengths (*d*) and bond angles (ω) for **1** × 0.5C_6H_5Me (**2**)

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Co(1)–N(5)	1.9893(13)	C(1)–C(3)	1.387(2)	Co(1)–N(7)	2.0032(13)	C(4)–C(5)	1.496(2)
Co(1)–N(3)	1.9935(13)	C(3)–C(4)	1.392(2)	Co(2)–N(4)	1.9956(13)	C(6)–C(7)	1.504(2)
Co(2)–O(1)	1.9506(12)	C(6)–C(8)	1.385(2)	Co(2)–N(9)	2.0278(13)	C(9)–C(10)	1.498(2)
Co(2)–N(2)	2.0183(13)	C(8)–C(9)	1.390(2)	Co(3)–N(8)	1.9794(13)	C(11)–C(12)	1.497(2)
Co(3)–O(3)	1.9219(12)	C(11)–C(13)	1.390(2)	Co(3)–N(11)	2.0199(12)	C(14)–C(15)	1.503(2)
Co(3)–N(6)	1.9798(13)	C(13)–C(14)	1.382(2)	O(2)–C(31)	1.234(2)	C(16)–C(17)	1.502(2)
O(1)–C(31)	1.2796(19)	C(16)–C(18)	1.390(2)	O(4)–C(33)	1.2342(19)	C(19)–C(20)	1.500(2)
O(3)–C(33)	1.286(2)	C(18)–C(19)	1.383(2)	N(1)–N(2)	1.3765(16)	C(21)–C(22)	1.497(2)
N(1)–C(1)	1.344(2)	C(21)–C(23)	1.399(2)	N(3)–C(6)	1.341(2)	C(24)–C(25)	1.495(2)
N(2)–C(4)	1.348(2)	C(23)–C(24)	1.375(2)	N(4)–C(9)	1.348(2)	C(26)–C(27)	1.498(2)
N(3)–N(4)	1.3833(16)	C(26)–C(28)	1.393(2)	N(5)–N(6)	1.3765(16)	C(29)–C(30)	1.498(2)
N(5)–C(11)	1.345(2)	C(28)–C(29)	1.372(2)	N(7)–C(16)	1.339(2)	C(33)–C(34)	1.510(2)
N(6)–C(14)	1.349(2)	C(31)–C(32)	1.504(3)	N(8)–C(19)	1.349(2)	C(35)–C(37)#1	1.401(3)
N(7)–N(8)	1.3801(16)	C(35)–C(36)	1.354(3)	N(9)–N(10)	1.3605(16)	C(37)–C(38)	1.335(5)
N(9)–C(21)	1.332(2)	C(36)–C(37)	1.400(3)	N(11)–C(26)	1.338(2)		
N(10)–C(24)	1.346(2)	C(37)–C(35)#1	1.401(3)	N(12)–C(29)	1.3493(19)		
N(11)–N(12)	1.3618(17)	Co(1)–N(1)	1.9916(13)	C(1)–C(2)	1.504(2)		
Angle	**ω, deg**	**Angle**	**ω, deg**	**Angle**	**ω, deg**	**Angle**	**ω, deg**
N(5)Co(1)N(1)	115.81(6)	N(12)N(11)Co(3)	122.14(10)	N(1)N(2)Co(2)	123.63(10)	C(18)C(16)C(17)	129.58(16)
N(1)Co(1)N(3)	108.54(5)	N(1)C(1)C(3)	109.71(13)	C(6)N(3)Co(1)	126.03(10)	C(19)C(18)C(16)	105.14(15)
N(1)Co(1)N(7)	107.27(5)	C(3)C(1)C(2)	129.35(15)	C(9)N(4)N(3)	107.58(12)	N(8)C(19)C(20)	121.20(15)
O(1)Co(2)N(4)	126.30(5)	N(2)C(4)C(3)	109.35(13)	N(3)N(4)Co(2)	121.87(10)	N(9)C(21)C(23)	110.07(14)
N(4)Co(2)N(2)	106.92(5)	C(3)C(4)C(5)	128.39(15)	C(11)N(5)Co(1)	125.40(10)	C(23)C(21)C(22)	129.36(16)
N(4)Co(2)N(9)	107.26(5)	N(3)C(6)C(7)	121.40(15)	C(14)N(6)N(5)	107.77(12)	N(10)C(24)C(23)	107.05(13)
O(3)Co(3)N(8)	107.59(5)	C(6)C(8)C(9)	105.38(15)	N(5)N(6)Co(3)	121.81(10)	C(23)C(24)C(25)	131.50(16)
N(8)Co(3)N(6)	108.62(5)	N(4)C(9)C(10)	122.25(14)	C(16)N(7)Co(1)	127.07(10)	N(11)C(26)C(27)	120.69(14)
N(8)Co(3)N(11)	111.10(5)	N(5)C(11)C(13)	109.19(14)	C(19)N(8)N(7)	107.66(13)	C(29)C(28)C(26)	106.40(15)
C(31)O(1)Co(2)	112.72(11)	C(13)C(11)C(12)	129.61(16)	N(7)N(8)Co(3)	124.43(10)	N(12)C(29)C(30)	121.52(16)
C(1)N(1)N(2)	107.99(12)	N(6)C(14)C(13)	109.46(13)	C(21)N(9)Co(2)	128.51(10)	O(2)C(31)O(1)	121.90(17)
N(2)N(1)Co(1)	124.24(10)	C(13)C(14)C(15)	129.29(16)	C(24)N(10)N(9)	111.06(13)	O(1)C(31)C(32)	116.36(16)
C(4)N(2)Co(2)	128.46(10)	N(7)C(16)C(17)	120.73(14	C(26)N(11)Co(3)	131.43(11)	O(4)C(33)C(34)	120.03(16)
C(6)N(3)N(4)	108.09(13)	N(5)Co(1)N(3)	109.19(5)	C(29)N(12)N(11)	110.85(14)	N(8)C(19)C(18)	109.58(14)
N(4)N(3)Co(1)	124.78(10)	N(5)Co(1)N(7)	107.98(5)	N(1)C(1)C(2)	120.94(14)	C(18)C(19)C(20)	129.22(16)
C(9)N(4)Co(2)	130.07(10)	N(3)Co(1)N(7)	107.77(5)	C(1)C(3)C(4)	105.06(14)	N(9)C(21)C(22)	120.55(14)
C(11)N(5)N(6)	108.11(13)	O(1)Co(2)N(2)	100.88(5)	N(2)C(4)C(5)	122.23(14)	C(24)C(23)C(21)	105.80(15)
N(6)N(5)Co(1)	125.24(10)	O(1)Co(2)N(9)	107.70(5)	N(3)C(6)C(8)	109.57(13)	N(10)C(24)C(25)	121.45(16)
C(14)N(6)Co(3)	128.63(10)	N(2)Co(2)N(9)	106.17(5)	C(8)C(6)C(7)	129.02(15)	N(11)C(26)C(28)	109.71(15)
C(16)N(7)N(8)	107.94(12)	O(3)Co(3)N(6)	119.15(5)	N(4)C(9)C(8)	109.38(14)	C(28)C(26)C(27)	129.60(16)
N(8)N(7)Co(1)	124.69(10)	O(3)Co(3)N(11)	99.47(5)	C(8)C(9)C(10)	128.36(15)	N(12)C(29)C(28)	106.89(14)
C(19)N(8)Co(3)	127.88(10)	N(6)Co(3)N(11)	110.60(5)	N(5)C(11)C(12)	121.20(15)	C(28)C(29)C(30)	131.58(15)
C(21)N(9)N(10)	106.02(12)	C(33)O(3)Co(3)	139.48(11)	C(14)C(13)C(11)	105.47(15)	O(2)C(31)C(32)	121.74(17)
N(10)N(9)Co(2)	125.44(10)	C(1)N(1)Co(1)	127.75(10)	N(6)C(14)C(15)	121.25(14)	O(4)C(33)O(3)	122.11(16)
C(26)N(11)N(12)	106.13(12)	C(4)N(2)N(1)	107.89(12)	N(7)C(16)C(18)	109.67(14)	O(3)C(33)C(34)	117.86(15)

Table 6. Coordinates of atoms ($\times 10^4$) and their equivalent isotropic factors ($Å^2 \times 10^3$) for complex $\mathbf{1} \times 0.5C_6H_6$ (**3**)

Atom	x	y	z	U_{eq}
Co(1)	3784(1)	8140(1)	1739(1)	41(1)
Co(2)	6289(1)	8006(1)	1205(1)	46(1)
Co(3)	1241(1)	7829(1)	2207(1)	47(1)
O(1)	6704(2)	6933(2)	1232(2)	63(1)
O(2)	7957(2)	7300(2)	1963(2)	85(1)
O(3)	207(2)	7510(2)	1489(2)	79(1)
O(4)	–777(3)	6966(2)	689(2)	94(1)
N(1)	5056(2)	8514(2)	2272(2)	48(1)
N(2)	5973(2)	8582(2)	2028(2)	47(1)
N(3)	4043(2)	8009(2)	774(2)	44(1)
N(4)	4992(2)	7954(2)	567(2)	46(1)
N(5)	2726(2)	8963(2)	1763(2)	43(1)
N(6)	1754(2)	8828(2)	1913(2)	44(1)
N(7)	3317(2)	7219(2)	2202(2)	45(1)
N(8)	2421(2)	7166(2)	2492(2)	46(1)
N(9)	7290(2)	8640(2)	741(2)	49(1)
N(10)	8215(2)	8399(2)	608(2)	52(1)
N(11)	407(2)	7976(2)	2988(2)	48(1)
N(12)	–538(2)	7673(2)	2990(2)	53(1)
C(1)	5126(3)	8869(2)	2879(2)	52(1)
C(2)	4247(3)	8891(3)	3285(2)	81(2)
C(3)	6077(3)	9161(3)	3025(2)	59(1)
C(4)	6601(3)	8978(2)	2491(2)	50(1)
C(5)	7674(3)	9161(3)	2395(3)	69(1)
C(6)	3360(3)	7939(2)	224(2)	47(1)
C(7)	2246(3)	7960(3)	275(2)	78(2)
C(8)	3851(3)	7837(2)	–333(2)	54(1)
C(9)	4869(3)	7834(2)	–109(2)	51(1)
C(10)	5746(3)	7724(3)	–503(2)	79(2)
C(11)	2789(3)	9687(3)	1568(2)	50(1)
C(12)	3757(3)	10008(3)	1367(3)	74(1)
C(13)	1864(3)	10039(3)	1580(2)	62(1)
C(14)	1249(3)	9492(3)	1803(2)	52(1)
C(15)	137(3)	9541(3)	1929(3)	87(2)
C(16)	3890(3)	6616(3)	2410(2)	59(1)
C(17)	4915(3)	6509(3)	2181(3)	90(2)
C(18)	3390(3)	6171(3)	2844(2)	67(1)
C(19)	2488(3)	6531(3)	2887(2)	53(1)
C(20)	1646(3)	6292(3)	3288(3)	81(2)
C(21)	7189(3)	9346(3)	493(2)	51(1)
C(22)	6252(3)	9805(3)	538(2)	70(1)
C(23)	8058(3)	9552(3)	206(2)	59(1)
C(24)	8690(3)	8938(3)	287(2)	51(1)
C(25)	9725(3)	8803(3)	76(3)	79(2)
C(26)	649(3)	8288(3)	3601(2)	59(1)
C(27)	1614(3)	8692(3)	3790(2)	81(2)
C(28)	–134(3)	8168(3)	3987(2)	69(1)
C(29)	–891(3)	7782(3)	3586(2)	58(1)
C(30)	–1915(3)	7515(3)	3706(3)	85(2)
C(31)	7462(3)	6784(3)	1658(3)	57(1)
C(32)	7727(4)	5956(3)	1763(3)	111(2)
C(33)	–76(5)	6929(5)	1179(5)	141(2)
C(34)	407(5)	6236(4)	1337(4)	141(2)
C(35)	2510(10)	5657(6)	820(4)	164(8)
C(36)	3406(10)	5874(4)	573(6)	101(5)
C(37)	3831(7)	5404(8)	115(5)	121(5)
C(38)	3362(10)	4716(7)	–96(4)	109(5)
C(39)	2466(10)	4499(4)	150(6)	119(5)
C(40)	2041(6)	4970(8)	608(6)	120(4)

Table 7. Bond lengths (*d*) and bond angles (ω) for $\mathbf{1} \times 0.5C_6H_6$

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Co(1)–N(7)	1.980(3)	N(10)–C(24)	1.332(5)	Co(1)–N(1)	1.992(3)	N(11)–C(26)	1.335(5)
Co(1)–N(3)	1.995(3)	N(11)–N(12)	1.362(4)	Co(1)–N(5)	2.010(3)	N(12)–C(29)	1.332(5)
Co(2)–O(1)	1.945(3)	C(1)–C(3)	1.361(5)	Co(2)–N(2)	1.998(3)	C(1)–C(2)	1.495(5)
Co(2)–N(4)	2.014(3)	C(3)–C(4)	1.372(6)	Co(2)–N(9)	2.028(3)	C(4)–C(5)	1.495(5)
Co(3)–O(3)	1.938(3)	C(6)–C(8)	1.356(5)	Co(3)–N(8)	1.974(3)	C(6)–C(7)	1.495(5)
Co(3)–N(6)	1.980(3)	C(8)–C(9)	1.373(5)	Co(3)–N(11)	2.020(3)	C(9)–C(10)	1.489(5)
O(1)–C(31)	1.261(5)	C(11)–C(13)	1.376(5)	O(2)–C(31)	1.229(5)	C(11)–C(12)	1.497(5)
O(3)–C(33)	1.218(7)	C(13)–C(14)	1.361(5)	O(4)–C(33)	1.266(8)	C(14)–C(15)	1.529(5)
N(1)–C(1)	1.346(5)	C(16)–C(18)	1.383(5)	N(1)–N(2)	1.367(4)	C(16)–C(17)	1.496(5)
N(2)–C(4)	1.352(5)	C(18)–C(19)	1.364(5)	N(3)–C(6)	1.338(4)	C(19)–C(20)	1.504(5)
N(3)–N(4)	1.374(4)	C(21)–C(23)	1.393(5)	N(4)–C(9)	1.344(5)	C(21)–C(22)	1.490(5)
N(5)–C(11)	1.323(5)	C(23)–C(24)	1.356(5)	N(5)–N(6)	1.379(4)	C(24)–C(25)	1.501(5)
N(6)–C(14)	1.340(5)	C(26)–C(28)	1.377(5)	N(7)–C(16)	1.332(5)	C(26)–C(27)	1.472(6)
N(7)–N(8)	1.385(4)	C(28)–C(29)	1.381(6)	N(8)–C(19)	1.349(5)	C(29)–C(30)	1.483(5)
N(9)–C(21)	1.323(5)	C(31)–C(32)	1.492(7)	N(9)–N(10)	1.353(4)	C(33)–C(34)	1.383(8)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
N(7)Co(1)N(1)	108.16(13)	N(10)N(9)Co(2)	125.4(3)	C(33)O(3)Co(3)	139.1(5)	C(14)C(13)C(11)	105.4(4)
N(1)Co(1)N(3)	108.20(13)	C(26)N(11)N(12)	106.0(3)	C(1)N(1)Co(1)	126.0(3)	N(6)C(14)C(15)	119.8(4)
N(7)Co(1)N(3)	116.76(13)	N(12)N(11)Co(3)	122.9(3)	C(4)N(2)N(1)	108.0(3)	N(7)C(16)C(18)	109.5(4)
N(7)Co(1)N(5)	107.89(13)	N(1)C(1)C(3)	109.0(4)	N(1)N(2)Co(2)	121.7(2)	C(18)C(16)C(17)	129.8(4)
N(1)Co(1)N(5)	107.90(13)	C(3)C(1)C(2)	129.8(4)	C(6)N(3)Co(1)	127.8(2)	N(8)C(19)C(18)	109.8(4)
O(1)Co(2)N(2)	122.99(13)	N(2)C(4)C(3)	108.2(3)	C(9)N(4)N(3)	107.4(3)	C(18)C(19)C(20)	128.3(4)
N(2)Co(2)N(4)	106.69(13)	C(3)C(4)C(5)	128.8(4)	N(3)N(4)Co(2)	123.9(2)	N(9)C(21)C(22)	121.6(4)
N(2)Co(2)N(9)	108.01(14)	N(3)C(6)C(7)	121.6(3)	C(11)N(5)Co(1)	127.1(3)	C(23)C(21)C(22)	128.7(4)
O(3)Co(3)N(8)	120.87(14)	C(6)C(8)C(9)	106.7(4)	C(14)N(6)N(5)	106.4(3)	N(10)C(24)C(23)	106.7(3)
N(8)Co(3)N(6)	107.86(13)	N(4)C(9)C(10)	122.0(4)	N(5)N(6)Co(3)	125.2(2)	C(23)C(24)C(25)	131.7(4)
N(8)Co(3)N(11)	110.10(13)	N(5)C(11)C(13)	109.3(4)	C(16)N(7)Co(1)	125.5(3)	N(11)C(26)C(27)	122.3(4)
C(31)O(1)Co(2)	114.6(3)	C(13)C(11)C(12)	129.5(4)	C(19)N(8)N(7)	107.1(3)	C(26)C(28)C(29)	107.5(4)
C(1)N(1)N(2)	107.8(3)	N(6)C(14)C(13)	110.2(4)	N(7)N(8)Co(3)	122.4(2)	N(12)C(29)C(30)	121.5(4)
N(2)N(1)Co(1)	125.3(3)	C(13)C(14)C(15)	130.0(4)	C(21)N(9)Co(2)	128.9(3)	O(2)C(31)O(1)	121.2(5)
C(4)N(2)Co(2)	129.4(3)	N(7)C(16)C(17)	120.8(4)	C(24)N(10)N(9)	111.6(3)	O(1)C(31)C(32)	116.6(5)
C(6)N(3)N(4)	108.1(3)	C(19)C(18)C(16)	105.8(4)	C(26)N(11)Co(3)	130.7(3)	O(3)C(33)C(34)	120.1(7)
N(4)N(3)Co(1)	124.1(2)	N(8)C(19)C(20)	122.0(4)	C(29)N(12)N(11)	111.7(3)	C(24)C(23)C(21)	106.4(4)
C(9)N(4)Co(2)	128.7(2)	N(9)C(21)C(23)	109.7(4)	N(1)C(1)C(2)	121.1(4)	N(10)C(24)C(25)	121.6(4)
C(11)N(5)N(6)	108.5(3)	N(3)Co(1)N(5)	107.64(12)	C(1)C(3)C(4)	107.0(4)	N(11)C(26)C(28)	109.1(4)
N(6)N(5)Co(1)	124.0(2)	O(1)Co(2)N(4)	101.10(13)	N(2)C(4)C(5)	122.9(4)	C(28)C(26)C(27)	128.6(5)
C(14)N(6)Co(3)	128.3(3)	O(1)Co(2)N(9)	109.55(13)	N(3)C(6)C(8)	109.1(3)	N(12)C(29)C(28)	105.6(4)
C(16)N(7)N(8)	107.9(3)	N(4)Co(2)N(9)	107.38(13)	C(8)C(6)C(7)	129.2(4)	C(28)C(29)C(30)	132.8(4)
N(8)N(7)Co(1)	125.3(2)	O(3)Co(3)N(6)	105.91(14)	N(4)C(9)C(8)	108.7(3)	O(2)C(31)C(32)	122.2(5)
C(19)N(8)Co(3)	129.7(3)	O(3)Co(3)N(11)	101.09(14)	C(8)C(9)C(10)	129.3(4)	O(3)C(33)O(4)	119.9(7)
C(21)N(9)N(10)	105.6(3)	N(6)Co(3)N(11)	110.70(13)	N(5)C(11)C(12)	121.1(4)	O(4)C(33)C(34)	119.9(7)

Table 8. Coordinates of atoms ($\times 10^4$) and their equivalent isotropic factors ($Å^2 \times 10^3$) for complex $\mathbf{4} \times C_6H_6$

Atom	x	y	z	U_{eq}
Zn(1)	38(1)	7516(1)	4854(1)	46(1)
Zn(2)	24(1)	8284(1)	6893(1)	55(1)
Zn(3)	–439(1)	6812(1)	2779(1)	55(1)
O(1)	–791(6)	9452(3)	7276(3)	80(1)
O(2)	–1438(7)	9690(5)	8362(3)	125(3)
O(3)	–2442(5)	5975(3)	2114(3)	80(2)
O(4)	–2989(6)	5974(5)	954(3)	109(2)
N(1)	1940(6)	8205(4)	5732(3)	49(2)
N(2)	1952(6)	8454(4)	6500(3)	54(2)
N(3)	–1692(6)	7123(4)	5269(3)	51(2)
N(4)	–1691(6)	7405(4)	6040(3)	47(2)
N(5)	–929(6)	8190(4)	4245(3)	46(2)
N(6)	–1095(6)	7947(4)	3454(3)	48(2)
N(7)	809(5)	6410(4)	4146(3)	44(2)
N(8)	708(6)	6166(4)	3373(3)	54(2)
N(9)	705(6)	7922(5)	7794(3)	66(2)
N(10)	518(7)	8455(4)	8512(3)	69(2)
N(11)	909(8)	6890(4)	2031(3)	61(2)
N(12)	179(7)	6574(4)	1256(3)	65(2)
C(1)	3429(9)	8448(5)	5670(4)	51(2)
C(2)	3780(7)	8267(5)	4897(4)	71(2)
C(3)	4393(8)	8871(5)	6405(4)	58(2)
C(4)	3480(9)	8882(5)	6917(4)	53(2)
C(5)	3900(8)	9254(5)	7787(4)	78(3)
C(6)	–3031(9)	6518(5)	4844(4)	56(2)
C(7)	–3378(8)	6086(5)	3976(3)	72(2)
C(8)	–3893(8)	6430(5)	5351(4)	59(2)
C(9)	–3054(9)	6991(5)	6088(4)	52(2)
C(10)	–3452(8)	7166(5)	6851(4)	74(2)
C(11)	–1665(7)	8964(5)	4516(4)	55(2)
C(12)	–1704(8)	9408(5)	5363(4)	69(2)
C(13)	–2314(8)	9184(5)	3909(4)	71(2)
C(14)	–1935(8)	8545(5)	3267(4)	57(2)
C(15)	–2311(8)	8486(6)	2451(4)	88(3)
C(16)	1473(7)	5777(5)	4357(4)	50(2)
C(17)	1710(7)	5850(5)	5178(4)	64(2)
C(18)	1789(8)	5119(5)	3719(4)	68(2)
C(19)	1308(8)	5356(5)	3115(4)	66(2)
C(20)	1346(10)	4883(5)	2266(4)	106(3)
C(21)	1644(8)	7320(5)	7906(4)	60(2)
C(22)	2134(9)	6582(6)	7247(4)	95(3)
C(23)	1999(8)	7470(6)	8685(4)	73(3)
C(24)	1288(9)	8198(6)	9066(4)	75(3)
C(25)	1271(10)	8678(6)	9904(4)	111(4)
C(26)	2496(10)	7064(6)	2087(5)	75(3)
C(27)	3689(9)	7429(6)	2881(4)	114(4)
C(28)	2752(11)	6854(6)	1344(5)	84(3)
C(29)	1276(11)	6536(6)	826(5)	76(3)
C(30)	783(10)	6188(6)	–37(4)	116(4)
C(31)	–1336(10)	9893(7)	7832(5)	80(1)
C(32)	–1993(9)	10754(5)	7861(5)	103(3)
C(33)	–3226(10)	5717(7)	1435(5)	80(2)
C(34)	–4660(9)	5002(5)	1210(4)	112(4)
C(35)	–3406(8)	8718(8)	–592(7)	139(5)
C(36)	–3697(9)	9008(4)	148(7)	162(6)
C(37)	–3782(9)	8406(9)	488(3)	170(6)
C(38)	–3576(9)	7516(8)	89(7)	125(4)
C(39)	–3284(8)	7227(5)	–650(7)	142(5)
C(40)	–3199(7)	7828(10)	–991(3)	157(7)

Table 9. Bond lengths (*d*) and bond angles (ω) for **4** × C_6H_6

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Zn(1)–N(5)	1.977(5)	N(10)–C(24)	1.344(9)	Zn(1)–N(1)	2.000(5)	N(11)–C(26)	1.329(8)
Zn(1)–N(3)	2.003(6)	N(11)–N(12)	1.369(6)	Zn(1)–N(7)	2.006(5)	N(12)–C(29)	1.346(8)
Zn(2)–O(1)	1.953(5)	C(1)–C(3)	1.370(8)	Zn(2)–N(2)	1.980(6)	C(1)–C(2)	1.492(8)
Zn(2)–N(4)	1.984(5)	C(3)–C(4)	1.362(9)	Zn(2)–N(9)	2.027(6)	C(4)–C(5)	1.501(8)
Zn(3)–N(6)	1.970(5)	C(6)–C(8)	1.378(9)	Zn(3)–N(8)	1.972(6)	C(6)–C(7)	1.497(8)
Zn(3)–O(3)	1.999(5)	C(8)–C(9)	1.377(8)	Zn(3)–N(11)	2.045(6)	C(9)–C(10)	1.492(8)
O(1)–C(31)	1.217(8)	C(11)–C(13)	1.367(10)	O(2)–C(31)	1.209(11)	C(11)–C(12)	1.512(8)
O(3)–C(33)	1.233(8)	C(13)–C(14)	1.372(8)	O(4)–C(33)	1.207(10)	C(14)–C(15)	1.502(9)
N(1)–C(1)	1.347(7)	C(16)–C(18)	1.359(8)	N(1)–N(2)	1.370(6)	C(16)–C(17)	1.509(8)
N(2)–C(4)	1.371(7)	C(18)–C(19)	1.354(10)	N(3)–C(6)	1.363(7)	C(19)–C(20)	1.518(8)
N(3)–N(4)	1.371(6)	C(21)–C(23)	1.387(9)	N(4)–C(9)	1.358(7)	C(21)–C(22)	1.506(8)
N(5)–C(11)	1.379(7)	C(23)–C(24)	1.354(9)	N(5)–N(6)	1.391(6)	C(24)–C(25)	1.496(9)
N(6)–C(14)	1.334(8)	C(26)–C(28)	1.400(9)	N(7)–C(16)	1.345(8)	C(26)–C(27)	1.525(9)
N(7)–N(8)	1.365(6)	C(28)–C(29)	1.362(9)	N(8)–C(19)	1.367(8)	C(29)–C(30)	1.492(9)
N(9)–C(21)	1.327(9)	C(31)–C(32)	1.508(12)	N(9)–N(10)	1.358(6)	C(33)–C(34)	1.531(11)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
N(5)Zn(1)N(1)	113.6(2)	N(10)N(9)Zn(2)	120.7(5)	C(33)O(3)Zn(3)	136.4(6)	C(11)C(13)C(14)	106.0(7)
N(1)Zn(1)N(3)	109.4(2)	C(26)N(11)N(12)	105.7(6)	C(1)N(1)Zn(1)	126.3(5)	N(6)C(14)C(15)	121.2(7)
N(5)Zn(1)N(3)	109.5(2)	N(12)N(11)Zn(3)	118.9(5)	N(1)N(2)C(4)	107.0(5)	N(7)C(16)C(18)	108.1(6)
N(5)Zn(1)N(7)	108.7(2)	N(1)C(1)C(3)	107.6(6)	C(4)N(2)Zn(2)	128.4(5)	C(18)C(16)C(17)	130.4(7)
N(1)Zn(1)N(7)	108.23(19)	C(3)C(1)C(2)	131.1(7)	C(6)N(3)Zn(1)	126.4(5)	C(18)C(19)N(8)	109.0(6)
O(1)Zn(2)N(2)	105.6(2)	C(3)C(4)N(2)	108.0(6)	C(9)N(4)N(3)	107.6(5)	N(8)C(19)C(20)	119.9(8)
N(2)Zn(2)N(4)	110.3(2)	N(2)C(4)C(5)	120.7(7)	N(3)N(4)Zn(2)	123.9(4)	N(9)C(21)C(22)	122.1(7)
N(2)Zn(2)N(9)	110.5(2)	N(3)C(6)C(7)	121.4(7)	C(11)N(5)Zn(1)	126.3(5)	C(23)C(21)C(22)	128.2(8)
N(6)Zn(3)N(8)	112.2(2)	C(9)C(8)C(6)	107.1(7)	C(14)N(6)N(5)	107.3(5)	N(10)C(24)C(23)	104.8(7)
N(8)Zn(3)O(3)	103.1(2)	N(4)C(9)C(10)	121.6(6)	N(5)N(6)Zn(3)	122.4(4)	C(23)C(24)C(25)	132.1(8)
N(8)Zn(3)N(11)	109.2(2)	C(13)C(11)N(5)	109.1(6)	C(16)N(7)Zn(1)	125.0(4)	N(11)C(26)C(27)	119.8(7)
C(31)O(1)Zn(2)	136.2(6)	N(5)C(11)C(12)	120.3(7)	N(7)N(8)C(19)	106.3(6)	C(29)C(28)C(26)	107.9(7)
C(1)N(1)N(2)	109.2(5)	N(6)C(14)C(13)	110.8(7)	C(19)N(8)Zn(3)	129.6(5)	N(12)C(29)C(30)	121.9(8)
N(2)N(1)Zn(1)	124.4(4)	C(13)C(14)C(15)	128.0(8)	C(21)N(9)Zn(2)	133.2(5)	O(2)C(31)O(1)	125.6(10)
N(1)N(2)Zn(2)	124.5(4)	N(7)C(16)C(17)	121.4(6)	C(24)N(10)N(9)	112.9(6)	O(1)C(31)C(32)	118.2(10)
C(6)N(3)N(4)	108.6(5)	C(19)C(18)C(16)	107.5(7)	C(26)N(11)Zn(3)	134.5(5)	O(4)C(33)C(34)	118.7(8)
N(4)N(3)Zn(1)	125.0(4)	C(18)C(19)C(20)	131.1(7)	C(29)N(12)N(11)	111.9(7)	C(24)C(23)C(21)	108.0(8)
C(9)N(4)Zn(2)	128.5(5)	N(9)C(21)C(23)	109.7(6)	N(1)C(1)C(2)	121.3(6)	N(10)C(24)C(25)	123.1(8)
C(11)N(5)N(6)	106.8(6)	N(3)Zn(1)N(7)	107.2(2)	C(4)C(3)C(1)	108.2(7)	N(11)C(26)C(28)	109.0(7)
N(6)N(5)Zn(1)	126.8(4)	O(1)Zn(2)N(4)	109.9(2)	C(3)C(4)C(5)	131.2(7)	C(28)C(26)C(27)	131.2(8)
C(14)N(6)Zn(3)	129.7(5)	O(1)Zn(2)N(9)	108.2(2)	N(3)C(6)C(8)	107.9(6)	N(12)C(29)C(28)	105.5(8)
C(16)N(7)N(8)	109.1(5)	N(4)Zn(2)N(9)	112.0(2)	C(8)C(6)C(7)	130.7(7)	C(28)C(29)C(30)	132.6(8)
N(8)N(7)Zn(1)	125.9(4)	N(6)Zn(3)O(3)	109.5(2)	N(4)C(9)C(8)	108.8(6)	O(2)C(31)C(32)	116.3(9)
N(7)N(8)Zn(3)	123.4(4)	N(6)Zn(3)N(11)	116.1(2)	C(8)C(9)C(10)	129.6(7)	O(4)C(33)O(3)	127.2(9)
C(21)N(9)N(10)	104.7(6)	O(3)Zn(3)N(11)	105.8(2)	C(13)C(11)C(12)	130.6(7)	O(3)C(33)C(34)	114.1(9)

Table 10. Coordinates of atoms ($\times 10^4$) and their equivalent isotropic factors ($Å^2 \times 10^3$) for adduct **1** × Hdmpz (**5**)

Atom	*x*	*y*	*z*	U_{eq}
Co(1)	2187(1)	1653(1)	3540(1)	41(1)
Co(2)	366(1)	1589(1)	1949(1)	48(1)
Co(3)	3934(1)	2551(1)	5021(1)	51(1)
O(1)	304(2)	2609(2)	1280(2)	72(1)
O(2)	–755(2)	2412(3)	257(2)	81(1)
O(3)	3808(2)	3370(3)	5761(2)	75(1)
O(4)	5004(2)	3609(3)	6596(2)	99(2)
N(1)	1171(2)	2128(2)	3556(2)	45(1)
N(2)	472(2)	2129(3)	2924(2)	47(1)
N(3)	1944(2)	705(3)	2731(2)	45(1)
N(4)	1283(2)	777(3)	2079(2)	45(1)
N(5)	2743(2)	1020(3)	4526(2)	46(1)
N(6)	3408(2)	1363(3)	5069(2)	45(1)
N(7)	2876(2)	2633(3)	3404(2)	43(1)
N(8)	3431(2)	3083(3)	4002(2)	49(1)
N(9)	–609(2)	791(3)	1577(2)	49(1)
N(10)	–1196(2)	897(3)	890(2)	52(1)
N(11)	5084(2)	2335(3)	5197(2)	61(1)
N(12)	5673(3)	2737(3)	5773(2)	64(1)
N(13)	–2697(4)	2250(4)	–1070(3)	94(2)
N(14)	–2128(3)	2869(5)	–1044(3)	87(2)
C(1)	1006(3)	2505(4)	4102(3)	53(1)
C(2)	1614(3)	2623(4)	4874(2)	83(2)
C(3)	214(3)	2758(4)	3857(3)	63(2)
C(4)	–97(3)	2529(4)	3112(3)	54(1)
C(5)	–917(3)	2662(4)	2553(3)	77(2)
C(6)	2413(3)	37(3)	2622(3)	44(1)
C(7)	3184(3)	–219(3)	3214(3)	68(2)
C(8)	2054(3)	–320(3)	1914(3)	56(2)
C(9)	1359(3)	161(4)	1600(3)	51(2)
C(10)	757(3)	72(3)	835(2)	77(2)
C(11)	1790(3)	–279(4)	4331(3)	89(2)
C(12)	2512(3)	258(4)	4786(3)	59(2)
C(13)	3041(3)	87(4)	5502(3)	71(2)
C(14)	3583(3)	783(4)	5658(3)	58(2)
C(15)	4290(3)	986(4)	6360(2)	98(2)
C(16)	3734(3)	3803(4)	3744(3)	61(2)
C(17)	4387(3)	4423(4)	4265(3)	97(2)
C(18)	3383(3)	3821(4)	2980(3)	63(2)
C(19)	2857(3)	3095(4)	2793(3)	52(2)
C(20)	2324(3)	2802(4)	2019(2)	88(2)
C(21)	–847(3)	74(4)	1878(3)	54(2)
C(22)	–337(3)	–247(3)	2646(3)	77(2)
C(23)	–1564(3)	–257(4)	1395(3)	62(2)
C(24)	–1775(3)	273(4)	773(3)	60(2)
C(25)	–2476(3)	235(4)	55(3)	92(2)
C(26)	5429(3)	1921(4)	4788(3)	76(2)
C(27)	4956(3)	1409(5)	4103(3)	150(4)
C(28)	6231(3)	2065(4)	5102(3)	88(2)
C(29)	6368(3)	2586(4)	5711(3)	67(2)
C(30)	7123(3)	2943(4)	6286(3)	105(2)
C(31)	–170(3)	2837(4)	632(3)	54(2)
C(32)	57(3)	3728(3)	340(3)	73(2)
C(33)	4304(4)	3681(4)	6390(3)	75(1)
C(34)	3938(3)	4136(4)	6867(3)	115(3)
C(35)	–3313(4)	2535(6)	–1649(4)	83(2)
C(36)	–4059(4)	1959(5)	–1845(4)	141(3)
C(37)	–3153(5)	3320(6)	–1971(3)	99(2)
C(38)	–2374(5)	3520(5)	–1571(4)	88(2)
C(39)	–1843(3)	4286(5)	–1635(3)	107(2)

Table 11. Bond lengths (*d*) and bond angles (ω) for **1** × Hdmpz (**5**)

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Co(1)–N(7)	1.971(4)	N(13)–C(35)	1.321(7)	Co(1)–N(1)	1.986(4)	N(13)–N(14)	1.355(6)
Co(1)–N(3)	1.997(4)	N(14)–C(38)	1.333(7)	Co(1)–N(5)	2.013(4)	C(1)–C(3)	1.391(6)
Co(2)–O(1)	1.932(3)	C(1)–C(2)	1.502(5)	Co(2)–N(4)	1.978(4)	C(3)–C(4)	1.379(6)
Co(2)–N(2)	1.984(4)	C(4)–C(5)	1.496(5)	Co(2)–N(9)	2.010(4)	C(6)–C(8)	1.379(6)
Co(3)–O(3)	1.934(3)	C(6)–C(7)	1.491(5)	Co(3)–N(6)	1.976(4)	C(8)–C(9)	1.371(6)
Co(3)–N(8)	1.994(4)	C(9)–C(10)	1.484(6)	Co(3)–N(11)	2.020(4)	C(11)–C(12)	1.496(6)
O(1)–C(31)	1.273(5)	C(12)–C(13)	1.384(6)	O(2)–C(31)	1.207(5)	C(13)–C(14)	1.359(6)
O(3)–C(33)	1.296(5)	C(14)–C(15)	1.513(6)	O(4)–C(33)	1.191(6)	C(16)–C(17)	1.527(6)
N(1)–C(1)	1.320(5)	C(16)–C(18)	1.376(6)	N(1)–N(2)	1.399(4)	C(18)–C(19)	1.370(6)
N(2)–C(4)	1.352(5)	C(19)–C(20)	1.511(6)	N(3)–C(6)	1.355(5)	C(21)–C(22)	1.503(6)
N(3)–N(4)	1.386(4)	C(21)–C(23)	1.378(6)	N(4)–C(9)	1.327(5)	C(23)–C(24)	1.354(6)
N(5)–C(12)	1.337(6)	C(24)–C(25)	1.497(6)	N(5)–N(6)	1.367(4)	C(26)–C(28)	1.374(6)
N(6)–C(14)	1.351(5)	C(26)–C(27)	1.479(6)	N(7)–C(19)	1.346(5)	C(28)–C(29)	1.340(7)
N(7)–N(8)	1.381(4)	C(29)–C(30)	1.501(6)	N(8)–C(16)	1.354(6)	C(31)–C(32)	1.518(6)
N(9)–C(21)	1.334(6)	C(33)–C(34)	1.481(7)	N(9)–N(10)	1.369(4)	C(35)–C(37)	1.372(8)
N(10)–C(24)	1.338(5)	C(35)–C(36)	1.516(8)	N(11)–C(26)	1.325(6)	C(37)–C(38)	1.370(8)
N(11)–N(12)	1.355(4)	C(38)–C(39)	1.502(8)	N(12)–C(29)	1.337(6)		
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
N(7)Co(1)N(1)	113.84(15)	C(3)C(1)C(2)	126.6(5)	C(16)N(8)N(7)	108.7(4)	O(2)C(31)O(1)	125.8(5)
N(1)Co(1)N(3)	108.22(16)	N(2)C(4)C(3)	109.2(4)	N(7)N(8)Co(3)	125.0(3)	O(1)C(31)C(32)	113.9(5)
N(1)Co(1)N(5)	106.37(15)	C(3)C(4)C(5)	129.4(5)	C(21)N(9)Co(2)	132.3(4)	O(4)C(33)C(34)	120.5(6)
O(1)Co(2)N(4)	111.45(16)	N(3)C(6)C(7)	121.5(4)	C(24)N(10)N(9)	111.7(4)	N(13)C(35)C(37)	112.5(7)
N(4)Co(2)N(2)	109.47(16)	C(9)C(8)C(6)	105.6(5)	C(26)N(11)Co(3)	131.7(4)	C(37)C(35)C(36)	131.2(8)
N(4)Co(2)N(9)	107.66(16)	N(4)C(9)C(10)	121.7(5)	C(29)N(12)N(11)	110.1(5)	N(14)C(38)C(37)	105.5(7)
O(3)Co(3)N(6)	107.18(15)	N(5)C(12)C(13)	108.9(5)	C(38)N(14)N(13)	113.4(6)	C(37)C(38)C(39)	132.2(8)
N(6)Co(3)N(8)	108.99(16)	C(13)C(12)C(11)	129.0(6)	N(1)C(1)C(2)	122.7(5)	N(6)C(14)C(15)	119.6(5)
N(6)Co(3)N(11)	110.60(16)	N(7)Co(1)N(3)	110.21(15)	C(4)C(3)C(1)	105.2(5)	N(8)C(16)C(18)	108.7(5)
C(31)O(1)Co(2)	134.9(3)	N(7)Co(1)N(5)	109.25(15)	N(2)C(4)C(5)	121.4(5)	C(18)C(16)C(17)	129.4(5)
C(1)N(1)N(2)	107.2(4)	N(3)Co(1)N(5)	108.78(16)	N(3)C(6)C(8)	109.1(4)	N(7)C(19)C(18)	111.0(4)
N(2)N(1)Co(1)	122.4(3)	O(1)Co(2)N(2)	107.71(15)	C(8)C(6)C(7)	129.3(5)	C(18)C(19)C(20)	127.0(5)
C(4)N(2)Co(2)	127.8(3)	O(1)Co(2)N(9)	111.69(15)	N(4)C(9)C(8)	110.3(4)	N(9)C(21)C(22)	119.2(5)
C(6)N(3)N(4)	107.1(4)	N(2)Co(2)N(9)	108.82(16)	C(8)C(9)C(10)	128.0(5)	C(24)C(23)C(21)	106.9(5)
N(4)N(3)Co(1)	121.8(3)	O(3)Co(3)N(8)	111.31(15)	N(5)C(12)C(11)	122.1(5)	N(10)C(24)C(25)	121.8(5)
C(9)N(4)Co(2)	127.5(3)	O(3)Co(3)N(11)	111.92(16)	C(14)C(13)C(12)	105.5(5)	N(11)C(26)C(28)	109.6(5)
C(12)N(5)N(6)	108.6(4)	N(8)Co(3)N(11)	106.82(17)	N(6)C(14)C(13)	110.2(4)	C(28)C(26)C(27)	129.7(6)
N(6)N(5)Co(1)	123.6(3)	C(33)O(3)Co(3)	132.2(4)	C(13)C(14)C(15)	130.2(5)	N(12)C(29)C(28)	107.5(5)
C(14)N(6)Co(3)	127.3(4)	C(1)N(1)Co(1)	130.4(3)	N(8)C(16)C(17)	121.8(5)	C(28)C(29)C(30)	131.4(6)
C(19)N(7)N(8)	106.0(4)	C(4)N(2)N(1)	107.7(4)	C(19)C(18)C(16)	105.5(5)	O(2)C(31)C(32)	120.3(5)
N(8)N(7)Co(1)	121.7(3)	N(1)N(2)Co(2)	124.5(3)	N(7)C(19)C(20)	122.0(5)	O(4)C(33)O(3)	124.6(6)
C(16)N(8)Co(3)	123.9(3)	C(6)N(3)Co(1)	129.7(3)	N(9)C(21)C(23)	110.6(4)	O(3)C(33)C(34)	114.9(5)
C(21)N(9)N(10)	104.3(4)	C(9)N(4)N(3)	107.8(4)	C(23)C(21)C(22)	130.2(5)	N(13)C(35)C(36)	116.2(8)
N(10)N(9)Co(2)	123.4(3)	N(3)N(4)Co(2)	124.4(3)	N(10)C(24)C(23)	106.5(5)	C(38)C(37)C(35)	105.5(7)
C(26)N(11)N(12)	106.0(4)	C(12)N(5)Co(1)	127.6(4)	C(23)C(24)C(25)	131.7(5)	N(14)C(38)C(39)	122.2(8)
N(12)N(11)Co(3)	121.8(4)	C(14)N(6)N(5)	106.8(4)	N(11)C(26)C(27)	120.7(5)		
C(35)N(13)N(14)	103.0(6)	N(5)N(6)Co(3)	125.7(3)	C(29)C(28)C(26)	106.8(6)		
N(1)C(1)C(3)	110.7(4)	C(19)N(7)Co(1)	131.5(3)	N(12)C(29)C(30)	121.0(6)		

from the mother solution by decantation, washed with hexane, and dried in flowing argon. Yield: 0.063 g (90%).

For $C_{34}H_{50}Co_3N_{12}O_4$ anal. calcd., %: C, 47.07; H, 5.81; N, 19.37.

Found, %: C, 47.11; H, 5.78; N, 19.41.

IR spectrum (KBr), ν, cm^{-1}: 3588 w, 3428 m br, 2932 w, 2872 w, 1684 w, 1664 w, 1564 s, 1416 s, 1336 m, 1172 w, 1132 w, 1040 m, 936 w, 756 w, 676 m, 616 w, 428 w, 376 w, 316 w.

$Co_3(\mu\text{-dmpz})_4(Hdmpz)_2(OOCMe)_2$ ($1 \times 0.5C_6H_5Me$) (2). To 3,5-dimethylpyrazole (0.044 g, 0.46 mmol) in toluene (20 mL), cobalt acetate hydrate (0.1 g, 0.23 mmol) was added. The reaction mixture was boiled with stirring for 3 h at 110°C to complete dissolution. The resulting violet solution was reduced in volume to 10 mL and kept for 24 h at +5°C. Violet crystals were separated from the mother solution by decantation, washed with hexane, and dried in flowing argon. Yield: 0.062 g (85%).

For $C_{37.5}H_{53.5}Co_3N_{12}O_4$ anal. calcd.,%: C, 49.28; H, 5.92; N, 18.41.

Found, %: C, 49.32; H, 5.88; N, 18.44.

IR spectrum (KBr), ν, cm^{-1}: 3454 s, 3118 w, 2922 w, 2859 w, 1619 s, 1564 s, 1526 s, 1414 s, 1333 m, 1297 m, 1169 w, 1131 w, 1086 w, 1041 s, 937 w, 773 m, 738 m, 657 m, 613 w, 494 w, 468 w, 427 w.

$Co_3(\mu\text{-dmpz})_4(Hdmpz)_2(OOCMe)_2$ ($1 \times 0.5C_6H_6$) (3). (a) Cobalt acetate hydrate (0.1 g, 0.23 mmol) and Hdmpz (0.044 g, 0.46 mmol) were boiled in benzene (20 mL) for 3 h. The resulting violet solution was cooled to room temperature on an oil bath, separated by decantation from a pink jelly precipitate, reduced in volume to 5 mL, and kept at +5°C for 24 h. Violet crystals were separated from the mother solution by decantation, washed with cold hexane, and dried in flowing argon. Yield: 0.006 g (8%).

(b) A mixture of cobalt acetate hydrate (0.2 g, 0.46 mmol) and 3,5-dimethylpyrazole (0.088 g, 0.92 mmol) was kept for 2 h at 150°C. The mixture gradually changed from pink to violet. The solid product was washed with heptane (10 mL × 3) to remove unreacted Hdmpz and dissolved in hot benzene (20 mL). The resulting violet solution was reduced in volume to 5 mL and kept at +5°C for 24 h. Violet crystals were separated from the mother solution by decantation, washed with cold hexane, and dried in flowing argon. Yield: 0.049 g (35%).

For $C_{37}H_{53}Co_3N_{12}O_4$ anal. calcd.,%: C, 49.01; H, 5.89; N, 18.54.

Found, %: C, 48.98; H, 5.93; N, 18.57.

IR spectrum (KBr), ν, cm^{-1}: 3676 w, 3472 m br, 2924 w, 2852 w, 1716 w, 1660 w, 1564 m, 1528 m, 1480 w, 1416 m, 1332 w, 1300 w, 1136 w, 1040 m, 772 w, 744 w, 680 m, 624 w, 484 w, 428 w, 400 w, 356 m.

$Zn_3(\mu\text{-dmpz})_4(Hdmpz)_2(OOCMe)_2 \times C_6H_6$ (4). A mixture of zinc acetate hydrate (0.2 g, 0.9 mmol) and Hdmpz (0.173 g, 1.8 mmol) was kept for 2 h at 150°C. The resulting colorless solid product was washed with heptane (10 mL × 3) to remove unreacted Hdmpz and dissolved in hot benzene (20 mL). The resulting violet solution was reduced in volume to 5 mL and kept at +5°C for 24 h. Colorless crystals were separated from the mother solution by decantation, washed with cold hexane, and dried in flowing argon. Yield: 0.13 g (45%).

For $C_{40}H_{56}N_{12}O_4Zn_3$ anal. calcd.,%: C, 49.78; H, 5.85; N, 17.42.

Found, %: C, 49.74; H, 5.88; N, 17.46.

IR spectrum (KBr), ν, cm^{-1}: 3124 w, 2928 w, 2856 w, 1696 w, 1604 m, 1564 m, 1524 m, 1472 w, 1428 s, 1336 s, 1304 m, 1188 m, 1152 m, 1092 w, 1048 s, 1016 m, 900 m, 804 w, 772 s, 756 m, 744 m, 660 s, 592 w, 512 w, 428 m, 336 m.

$Co_3(\mu\text{-dmpz})_4(Hdmpz)_2(OOCMe)_2$ (1 × Hdmpz) (5). A mixture of cobalt acetate hydrate (0.2 g, 0.46 mmol) and 3,5-dimethylpyrazole (0.097 g, 1 mmol) was kept for 2 h at 150°C. The mixture gradually changed from pink to violet. The solid product was extracted by CH_2Cl_2 (15 mL), hexane (10 mL) was added, reduced in volume to 10 mL, and kept at 0°C for 24 h. Violet crystals were separated from the mother solution by decantation, washed with cold hexane, and dried in flowing argon. Yield: 0.059 g (40%).

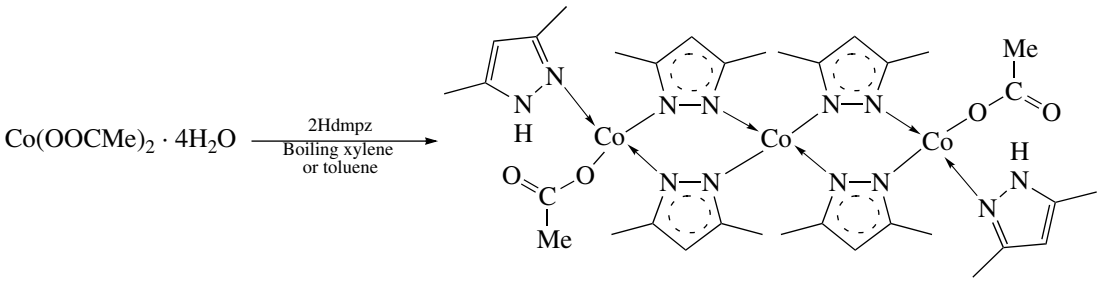
For $C_{39}H_{58}Co_3N_{14}O_4$ anal. calcd.,%: C, 48.60; H, 6.07; N, 20.35.

Found, %: C, 48.56; H, 6.11; N, 20.39.

IR spectrum (KBr), ν, cm^{-1}: 3425 w, 3236 m, 3124 w, 2924 w, 1660 w, 1564 s, 1524 s, 1460 w, 1408 s, 1324 s, 1296 s, 1184 m, 1132 m, 1088 w, 1040 s, 1016 m, 980 w, 932 w, 784 m, 756 m, 660 s, 588 w, 516 w, 448 w, 428 m, 360 m.

RESULTS AND DISCUSSION

We found that the reaction of hydrous cobalt acetates with 2 mol of 3,5-dimethylpyrazole in boiling xylene or toluene yields, in near-quantitative yield, violet trinuclear pyrazolate-bridged complex $Co_3(\mu\text{-dmpz})_6(Hdmpz)_2(OOCMe)_2$ (complex **1**) and its toluene solvate $\mathbf{1} \times 0.5C_6H_5Me$ (**2**), respectively:



When a mixture of crystalline cobalt or zinc acetate hydrate with Hdmpz in the ratio 1 : 2 is heated at 150°C for 2 h with subsequent elimination of unreacted pyrazole by hexane and recrystallization from benzene, the products are solvates of complex **1** with 0.5 C_6H_6 molecules and $Zn_3(\mu\text{-dmpz})_4(Hdmpz)_2(OOCMe)_2 \times C_6H_6$ (**4**), respectively. In the presence of excess Hdmpz, adduct **1** × Hdmpz (**5**) is formed; it was obtained by recrystallization from CH_2Cl_2/hexane.

X-ray crystallography shows that in complex **1** (Fig. 1; Tables 2, 3), the three cobalt atoms lying at nonbonded Co···Co distances (3.5976(9) and 3.6073(9) Å) and pyrazolate bridged with equalized Co–N distances (1.960(4)–2.005(4) Å), form a virtually linear metal core Co_3 (angle Co_2/Co_2 168.7°). The central cobalt atom is surrounded by a tetrahedral array of four nitrogen atoms from the bridging pyrazolate anions; the tetrahedral surrounding of the peripheral cobalt atoms is supplemented by the oxygen atoms of the terminal acetate anion (Co–O, 1.944(3), 2.005(4) Å) and the nitrogen atom of the terminal pyrazole molecule (Co–N, 1.944(3), 1.953(4) Å).

The appearance of solvating toluene molecules in crystals of complex **2** (Tables 3, 4) or benzene solvating molecules in complex **3** (Tables 5, 6) only insignificantly influences the geometry of a $Co_3(\mu\text{-dmpz})_6(Hdmpz)_2(OOCMe)_2$ molecule (Co···Co 3.6153(4), 3.6421(4) Å, Co–μ-N, 1.989(1)–2.018(1) Å; Co–O, 1.922(1), 1.951(1) Å; Co–N, 2.012(1), 2.028(1) Å; angle Co2/Co2 167.6° in complex **2**; and Co···Co 3.6170(9), 3.6481(9) Å, Co–μ-N, 1.980(3)–2.014(3) Å; Co–O, 1.938(3), 1.945(3) Å; Co–N, 2.020(3), 2.028(3) Å; angle Co_2/Co_2 173.8° in complex **3**).

In crystals of complexes **1**–**3**, the oxygen atoms of acetate anions and the hydrogen atoms of NH moieties in a molecule of complex **1** are linked by intermolecular hydrogen bonds to form 1-D polymers (N···O 2.763–2.908 Å); the character of these bonds, although having virtually identical geometry with close Co(2A)···Co(2B) distances (6.864, 6.572, 6.650 Å, respectively), in complex **1** (Fig. 2) differs from that in complexes **2** and **3** (Fig. 3), the last two complexes having solvating solvent molecules.

In complex **1** acetate anions form a staggered conformation (with the angle of 21.6° formed by C(31A)C(32A) and C(31B)C(32B) lines), whereas in formally looser unit cells containing solvating toluene or benzene molecules, the acetate ions are parallel and directed to one side.

We should mention that structure has recently been solved at room temperature for complex **1**, which was prepared in high yield by the thermolysis of cobalt acetate and 3,5-dimethylpyrazole at 130°C for 24 h followed by extraction with CH_2Cl_2 [6], and the geometry of this complex, including the character of intermolecular hydrogen bonds, completely matches the geometry of complex **1**, which was structurally studied at 120 K.

Unlike in complexes **1**–**3**, in zinc complex **4** (Fig. 4; Tables 8, 9), which has a similar geometry despite the presence of solvating benzene molecules, only short intramolecular hydrogen bonds were found (N···O 2.625, 2.693 Å, H···O 1.796 1.81 Å). In the trinuclear complex **4** with the Zn_3 metal core (Zn···Zn 3.622(1), 3.635(1) Å, Zn_2/Zn_2 173.2°), the central zinc atom is surrounded by a tetrahedral array of nitrogen atoms from four bridging pyrazolate anions (Zn–N, 1.977(5)–2.006(5) Å); the two peripheral zinc atoms have a tetrahedral surrounding, which includes, in addition to the nitrogen atoms of the bridging pyrazolate anions, the oxygen atom of the terminal acetate anion (Zn–O, 1.953(5), 1.999(5) Å) and the nitrogen atoms of the terminal pyrazole molecules (Zn–N, 2.027(6), 2.045(6) Å).

Finally, the substitution of the electron-deficient cobalt(II) atom for the electron-saturated zinc(II) atom practically does not affect the geometry of $M_3(\mu\text{-dmpz})_4(Hdmpz)_2(OOCMe)_2$ trinuclear complexes (possibly, except for the character of intermolecular hydrogen bonds), which was also shown by the comparison of geometries of dinuclear pyrazolate-bridged zinc and cobalt pivalates $M_2(\mu\text{-dmpz})_2(Hdmpz)_2(OOCBu^t)_2$ [7–10].

Possibly, the existence of intramolecular hydrogen bonds in trinuclear $Zn_3(\mu\text{-dmpz})_6(Hdmpz)_2(OOCMe)_2$ is responsible for the inhibited formation of $[Zn(dmpz)_2]_n$ polymer [1], in contrast to $[Zn(pz)_2]_n$ polymer. The latter

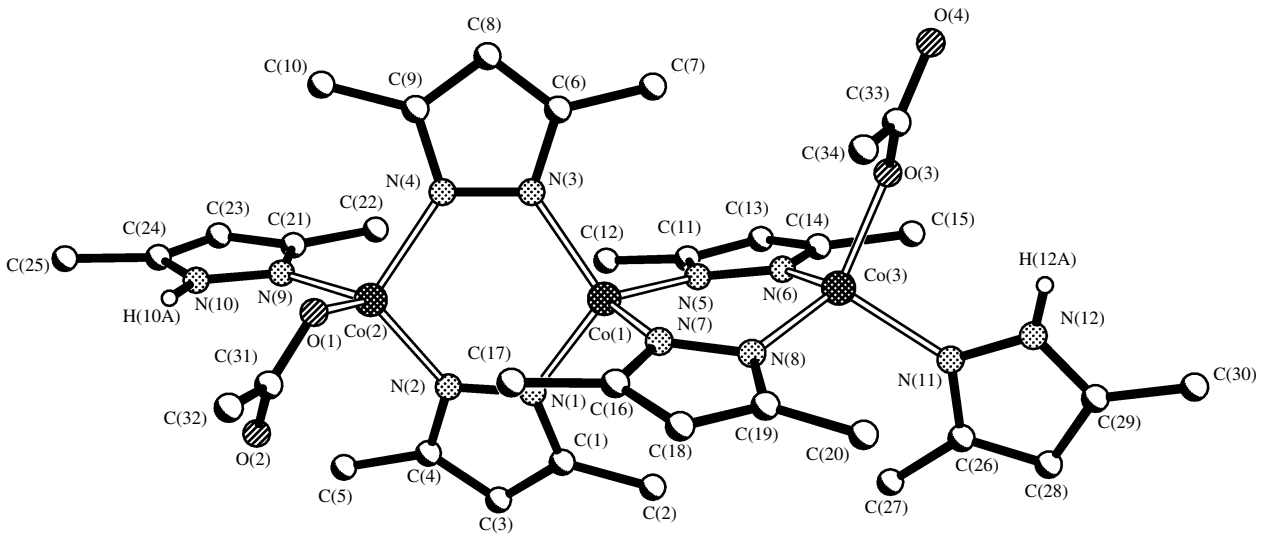


Fig. 1. Structure of complex **1**.

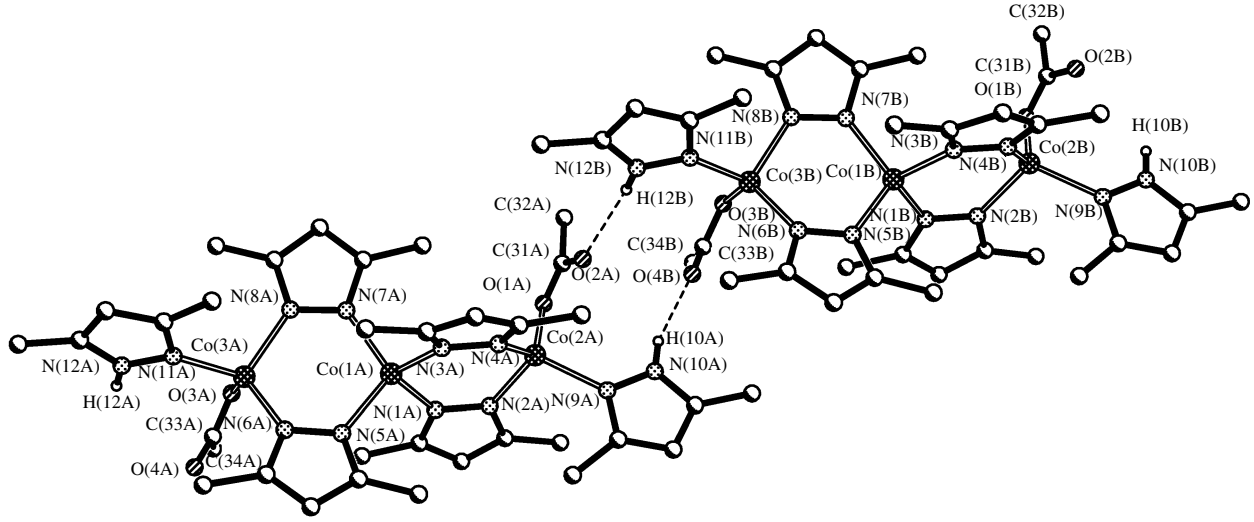


Fig. 2. Intermolecular hydrogen bonds in complex **1**.

is formed upon the thermolysis (220°C) of binuclear $Zn_2(\mu\text{-pz})_2(Hpz)_2(OOCMe)_2$, where X-ray crystallography detected intermolecular hydrogen bonds like those observed in complexes **1**–**3** [1].

Intramolecular hydrogen bonds are also observed in adduct **1** × Hdmpz (**5**). X-ray crystallography shows that in adduct **5** (Fig. 5; Tables 10, 11), the hydrogen atom of the NH moiety of the solvating Hdmpz molecule is hydrogen-bonded to the oxygen atom of the terminal acetate anion (N···O 2.886 Å; O···H 2.08 Å) belonging to trinuclear complex **1**, which is also linked via intramolecular hydrogen bond with the hydrogen atom of the coordinated pyrazole molecule (N···O 2.763 Å; O···H 1.96 Å; Co–O, 1.932(3) Å; Co–N, 2.010(4) Å). The geometry of the Co_3 molecule is another than in complex **1**: with close values of Co(1)···Co(2) (3.5901(9) Å) and Co(1)···Co(3) (3.6356(9) Å) nonbonded distances and the Co–μ-N (1.971(4)–2.013(4) Å) and Co(2,3)–N (2.010(4), 2.020(4) Å) bond lengths, the angle Co_2/Co_2 decreases to 160.7° and the oxygen atom of the terminal acetate anion and the hydrogen of the NH moiety of pyrazole, both coordinated to the Co(3) atom, form a short intramolecular hydrogen bond (O···N 2.658 Å; O···H 1.85 Å).

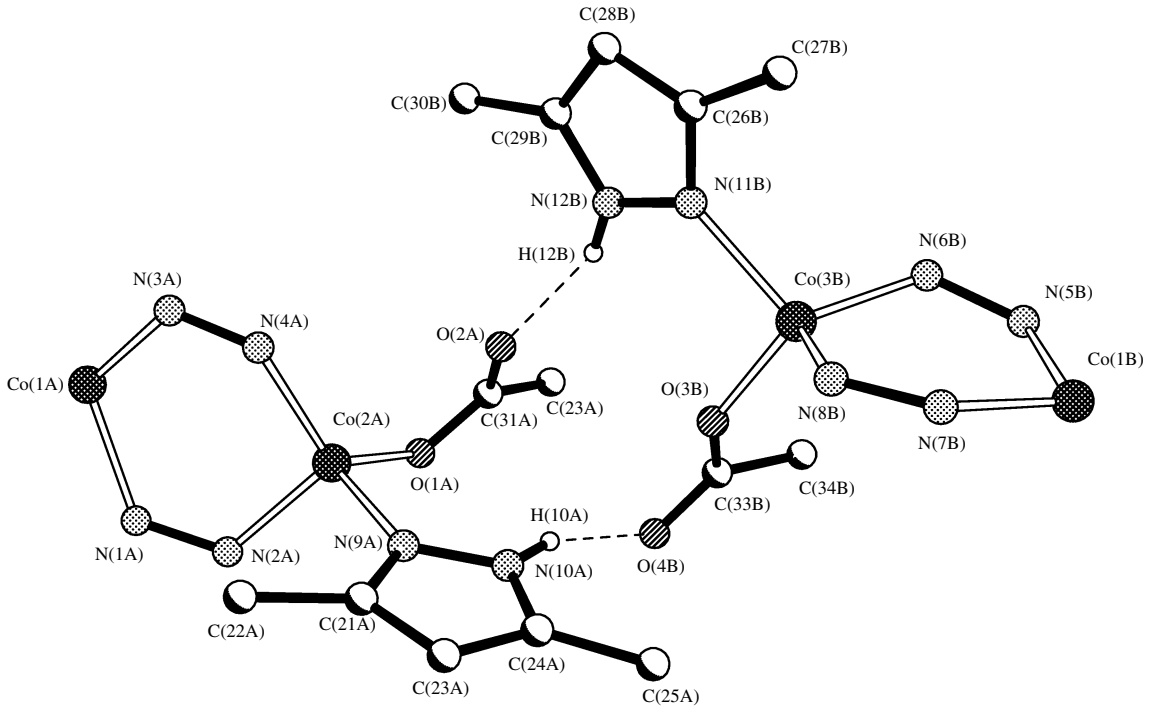


Fig. 3. Intermolecular hydrogen bonds in complexes **2** and **3** (only coordination cores for the Co(2) and Co(3) and basal nitrogen atoms of bridging pyrazolate anions are shown).

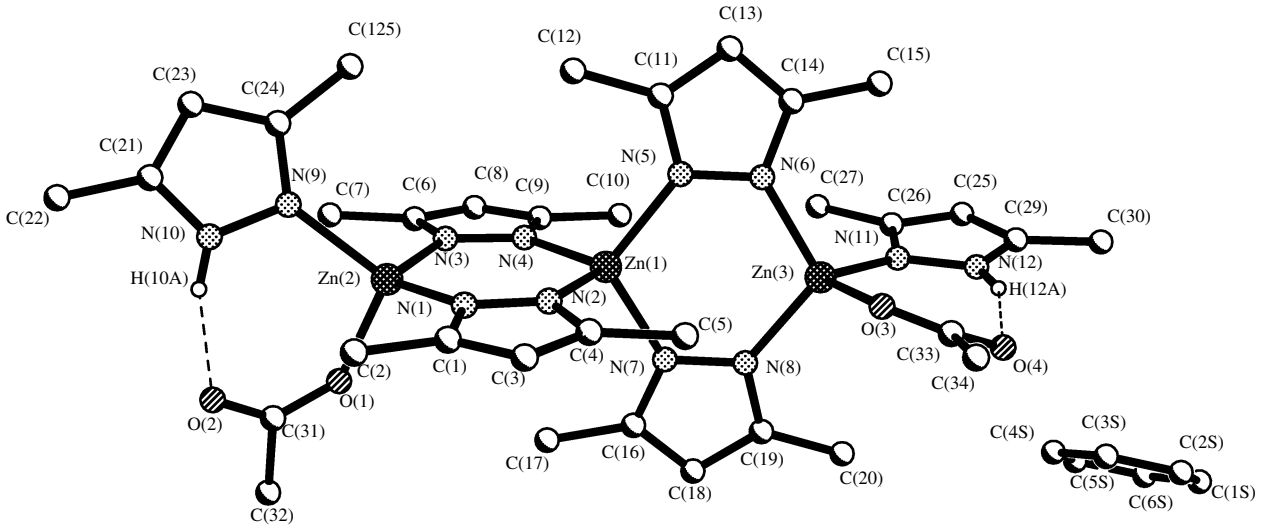


Fig. 4. Structure of complex **4** × C_6H_6.

To summarize, we discovered that, unlike zinc and cobalt pivalates which react with Hdmpz under mild conditions to yield pyrazolate-bridged dimers $M_2(\mu\text{-dmpz})_2(Hdmpz)_2(OOCBu^t)_2$, aqueous acetates in similar reactions upon heating to 150°C yield trinuclear pyrazolate-bridged complexes $M_3(\mu\text{-dmpz})_4(Hdmpz)_2(OOCMe)_2$, where the character of hydrogen bonding is dictated by the nature of the transition metal and the nature of solvating molecules.

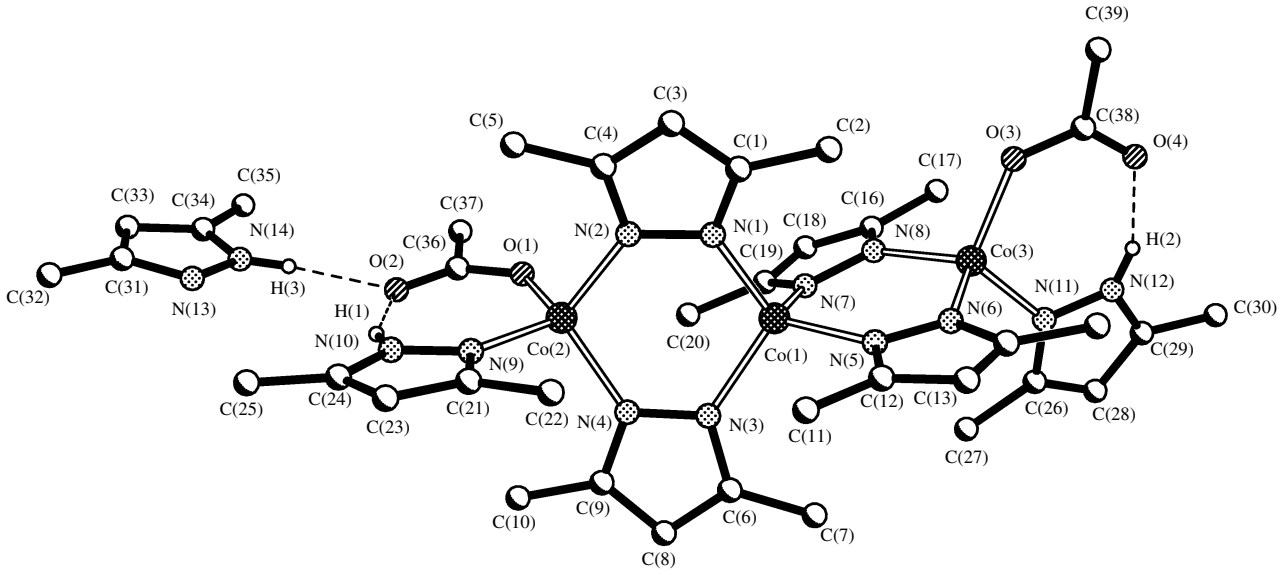


Fig. 5. Structure of adduct **1** × Hdmpz (**5**).

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