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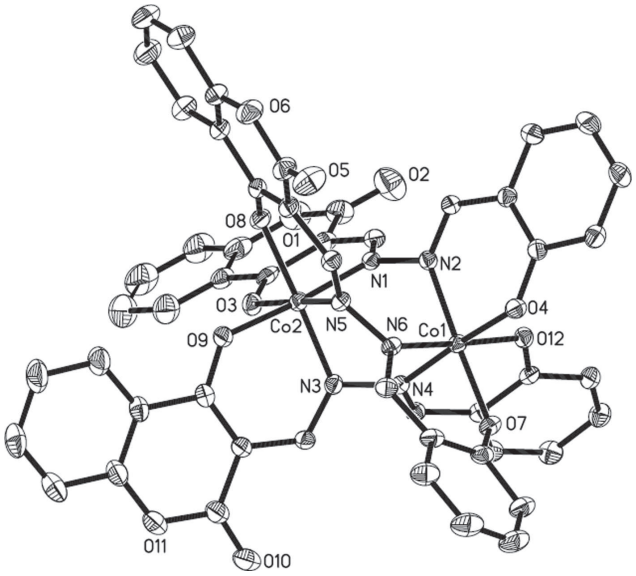
Crystal structure of tris{(3-(((*E*)-(((*E*)-2-oxidobenzylidene)hydrazono)methyl)-2-oxo-2*H*-chromen-4-olato-κ^3*O*,*N*:*N*′)}dicobalt(III)tris(dimethylformamide), $C_{60}H_{50}Co_2N_9O_{15}$



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Abstract

$C_{60}H_{50}Co_2N_9O_{15}$, triclinic, $P\bar{1}$ (no. 2), $a = 13.6074(19)$ Å, $b = 13.9185(17)$ Å, $c = 15.837(2)$ Å, $\alpha = 81.196(4)°$, $\beta = 86.607(4)°$, $\gamma = 81.665(4)°$, $Z = 2$, $V = 2930.7(7)$ Å^3, $R_{gt}(F) = 0.0564$, $wR_{ref}(F^2) = 0.2010$, $T = 296(2)$ K.

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The crystal structure is shown in the figure. Hydrogen atoms are omitted for clarity. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Brown block
Size:	0.28 × 0.26 × 0.22 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.64 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω-scans
θ_{max}, completeness:	27.8°, >98%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	26810, 13597, 0.035
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 8398
$N(param)_{refined}$:	780
Programs:	Bruker programs [1], SHELX [2]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Co1	0.29707(3)	0.39591(3)	0.36282(3)	0.03739(14)
Co2	0.24788(3)	0.22361(3)	0.24220(3)	0.03947(14)
N1	0.2981(2)	0.19628(18)	0.35421(17)	0.0384(6)
N2	0.3588(2)	0.26292(19)	0.37469(17)	0.0388(6)
N3	0.1520(2)	0.32578(19)	0.27517(17)	0.0401(6)
N4	0.1687(2)	0.35687(18)	0.35399(17)	0.0380(6)
N5	0.3398(2)	0.31539(19)	0.20886(17)	0.0401(6)
N6	0.3178(2)	0.40601(19)	0.24096(17)	0.0404(6)
N7	0.7995(5)	0.2300(6)	0.2652(4)	0.128(2)
N8	0.6315(4)	0.5677(4)	0.1271(3)	0.0930(14)
N9	0.5500(6)	0.8502(4)	0.3590(3)	0.1113(19)
O1	0.1305(3)	−0.0722(2)	0.4835(2)	0.0852(10)
O2	0.2451(3)	−0.0164(3)	0.5483(3)	0.1041(13)
O3	0.15410(19)	0.13375(17)	0.26877(16)	0.0496(6)
O4	0.41909(18)	0.44239(16)	0.37091(16)	0.0452(6)
O5	0.5964(3)	0.2781(3)	0.0656(2)	0.0873(10)
O6	0.6032(2)	0.1202(2)	0.0710(2)	0.0709(8)
O7	0.23504(19)	0.52707(17)	0.35712(16)	0.0478(6)
O8	0.3381(2)	0.11662(17)	0.21040(16)	0.0485(6)
O9	0.2033(2)	0.24234(18)	0.12866(15)	0.0499(6)
O10	−0.0815(3)	0.4775(3)	0.1418(2)	0.0904(11)
O11	−0.0518(3)	0.4022(3)	0.0294(2)	0.0816(10)
O12	0.28257(18)	0.38433(17)	0.48319(15)	0.0449(6)
O13	0.9140(4)	0.2759(5)	0.3404(4)	0.162(2)
O14	0.6519(10)	0.5563(8)	−0.0061(4)	0.311(7)
O15	0.5047(7)	1.0065(4)	0.3730(5)	0.228(4)
C1	0.0165(4)	0.0014(4)	0.2782(4)	0.0884(16)
H1	0.0187	0.0476	0.2293	0.106*
C2	−0.0501(5)	−0.0657(5)	0.2840(5)	0.113(2)
H2	−0.0913	−0.0656	0.2391	0.136*
C3	−0.0544(5)	−0.1335(4)	0.3582(6)	0.115(2)
H3	−0.0991	−0.1789	0.3630	0.138*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C4	0.0072(4)	−0.1340(4)	0.4245(5)	0.0966(19)
H4	0.0049	−0.1789	0.4743	0.116*
C5	0.0715(4)	−0.0662(3)	0.4143(4)	0.0709(13)
C6	0.0782(3)	0.0016(3)	0.3415(3)	0.0573(10)
C7	0.1499(3)	0.0705(2)	0.3367(3)	0.0488(9)
C8	0.2086(3)	0.0627(2)	0.4080(3)	0.0492(9)
C9	0.1973(4)	−0.0086(3)	0.4830(3)	0.0676(12)
C10	0.2766(3)	0.1280(2)	0.4143(2)	0.0466(8)
H10	0.3085	0.1216	0.4657	0.056*
C11	0.4495(3)	0.2286(2)	0.3931(2)	0.0426(8)
H11	0.4701	0.1618	0.3934	0.051*
C12	0.5194(3)	0.2873(3)	0.4130(2)	0.0451(8)
C13	0.6112(3)	0.2388(3)	0.4435(3)	0.0634(11)
H13	0.6253	0.1709	0.4470	0.076*
C14	0.6804(3)	0.2908(4)	0.4684(3)	0.0717(13)
H14	0.7408	0.2583	0.4889	0.086*
C15	0.6592(3)	0.3920(3)	0.4627(3)	0.0660(12)
H15	0.7049	0.4267	0.4818	0.079*
C16	0.5729(3)	0.4416(3)	0.4296(3)	0.0516(9)
H16	0.5620	0.5098	0.4243	0.062*
C17	0.4992(3)	0.3911(3)	0.4031(2)	0.0439(8)
C18	0.4719(3)	0.0320(3)	0.1400(2)	0.0547(10)
C19	0.4344(4)	−0.0565(3)	0.1571(3)	0.0677(12)
H19	0.3738	−0.0596	0.1869	0.081*
C20	0.4859(4)	−0.1405(4)	0.1302(3)	0.0816(15)
H20	0.4604	−0.1997	0.1429	0.098*
C21	0.5761(4)	−0.1360(4)	0.0841(4)	0.0842(15)
H21	0.6105	−0.1920	0.0652	0.101*
C22	0.6138(4)	−0.0484(4)	0.0668(4)	0.0838(15)
H22	0.6747	−0.0450	0.0374	0.101*
C23	0.5606(3)	0.0348(3)	0.0934(3)	0.0605(11)
C24	0.5553(3)	0.2082(3)	0.0910(3)	0.0599(10)
C25	0.4619(3)	0.2082(3)	0.1404(2)	0.0475(8)
C26	0.4191(3)	0.1221(3)	0.1656(2)	0.0467(9)
C27	0.4222(3)	0.2992(2)	0.1669(2)	0.0445(8)
H27	0.4589	0.3512	0.1526	0.053*
C28	0.3070(3)	0.4857(2)	0.1862(2)	0.0457(8)
H28	0.3174	0.4801	0.1285	0.055*
C29	0.2803(3)	0.5810(3)	0.2090(3)	0.0506(9)
C30	0.2843(4)	0.6619(3)	0.1433(3)	0.0690(12)
H30	0.3062	0.6512	0.0883	0.083*
C31	0.2559(4)	0.7563(3)	0.1603(4)	0.0816(15)
H31	0.2600	0.8094	0.1174	0.098*
C32	0.2211(4)	0.7715(3)	0.2420(4)	0.0807(15)
H32	0.2003	0.8353	0.2527	0.097*
C33	0.2166(3)	0.6954(3)	0.3070(3)	0.0627(11)
H33	0.1939	0.7085	0.3612	0.075*
C34	0.2459(3)	0.5971(3)	0.2934(3)	0.0485(9)
C35	0.1977(3)	0.3910(2)	0.5265(2)	0.0404(7)
C36	0.1967(3)	0.4095(3)	0.6120(2)	0.0516(9)
H36	0.2560	0.4173	0.6349	0.062*
C37	0.1119(3)	0.4162(3)	0.6619(2)	0.0584(10)
H37	0.1144	0.4286	0.7177	0.070*
C38	0.0214(3)	0.4049(3)	0.6309(2)	0.0562(10)
H38	−0.0364	0.4106	0.6652	0.067*
C39	0.0188(3)	0.3853(3)	0.5492(2)	0.0528(9)
H39	−0.0413	0.3764	0.5285	0.063*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C40	0.1058(3)	0.3782(2)	0.4952(2)	0.0408(7)
C41	0.0979(3)	0.3551(2)	0.4116(2)	0.0413(8)
H41	0.0381	0.3376	0.3977	0.050*
C42	0.0796(3)	0.3748(3)	0.2303(2)	0.0441(8)
H42	0.0383	0.4238	0.2539	0.053*
C43	0.0598(3)	0.3580(3)	0.1473(2)	0.0486(9)
C44	−0.0277(3)	0.4167(3)	0.1095(3)	0.0640(11)
C45	0.0068(4)	0.3377(3)	−0.0151(3)	0.0651(11)
C46	−0.0236(4)	0.3274(4)	−0.0953(3)	0.0864(16)
H46	−0.0831	0.3624	−0.1158	0.104*
C47	0.0331(5)	0.2665(5)	−0.1436(3)	0.0928(18)
H47	0.0127	0.2606	−0.1973	0.111*
C48	0.1210(5)	0.2132(5)	−0.1135(3)	0.0974(18)
H48	0.1593	0.1707	−0.1464	0.117*
C49	0.1514(4)	0.2234(4)	−0.0343(3)	0.0772(14)
H49	0.2113	0.1888	−0.0145	0.093*
C50	0.0943(3)	0.2840(3)	0.0158(2)	0.0568(10)
C51	0.1224(3)	0.2939(3)	0.1020(2)	0.0484(9)
C52	0.5205(9)	0.7562(6)	0.3572(5)	0.177(4)
H52A	0.5307	0.7165	0.4120	0.265*
H52B	0.5595	0.7248	0.3141	0.265*
H52C	0.4514	0.7642	0.3444	0.265*
C53	0.6513(9)	0.8570(7)	0.3377(7)	0.171(4)
H53A	0.6631	0.9236	0.3362	0.257*
H53B	0.6678	0.8371	0.2826	0.257*
H53C	0.6917	0.8149	0.3799	0.257*
C54	0.4869(8)	0.9286(6)	0.3740(5)	0.161(4)
H54	0.4212	0.9190	0.3868	0.194*
C55	0.5404(8)	0.5582(8)	0.1415(15)	0.346(13)
H55A	0.5036	0.5435	0.0987	0.415*
H55B	0.5105	0.5660	0.1948	0.415*
C56	0.6873(11)	0.5950(10)	0.1909(8)	0.266(8)
H56A	0.6427	0.6205	0.2339	0.399*
H56B	0.7267	0.6444	0.1650	0.399*
H56C	0.7301	0.5385	0.2166	0.399*
C57	0.6821(12)	0.5590(9)	0.0564(6)	0.230(7)
H57	0.7508	0.5545	0.0585	0.276*
C58	0.7449(9)	0.1497(7)	0.2553(5)	0.167(4)
H58A	0.7581	0.0975	0.3021	0.251*
H58B	0.7657	0.1258	0.2024	0.251*
H58C	0.6749	0.1730	0.2549	0.251*
C59	0.7533(11)	0.3227(10)	0.2224(10)	0.292(9)
H59A	0.7815	0.3749	0.2408	0.437*
H59B	0.6832	0.3300	0.2361	0.437*
H59C	0.7642	0.3249	0.1618	0.437*
C60	0.8652(6)	0.2193(7)	0.3198(5)	0.127(3)
H60	0.8780	0.1560	0.3493	0.153*

Source of material

Synthesis of the organic ligand: All reagents and starting materials were obtained from commercial suppliers and used as received. The educt for the organic ligand was synthesized according to an analogous method reported previously [3–5]. To an ethanol solution (5 mL) of 4-hydroxy-2-oxo-2*H*-chromene-3-carbaldehyde (190.2 mg, 1 mmol) was added an

ethanol solution (5 mL) of (*E*)-2-(hydrazonomethyl)phenol (136.2 mg, 1 mmol). The solution was stirred under reflux conditions at 434 K for 6 h. After cooling to room temperature, the precipitate was filtered and washed with ethanol and hexane. The product was dried under vacuum and we obtained a faint yellow solid (yield 71.2%, m.p. 542–543 K). Elemental analysis – Anal. Calcd. For $C_{17}H_{12}N_2O_4$ (%): C, 66.23; H, 3.92; N, 9.09. Found(%): C, 66.47; H, 3.83; N, 9.85.

Synthesis of the dinuclear cobalt(III) complex: An ethanol solution (2 mL) of cobalt acetate tetrahydrate (1.00 mg, 0.004 mmol) was added dropwise a solution of 4-hydroxy-3-((*E*)-(((*E*)-2-hydroxybenzylidene)hydrazono)methyl)-2H-chromen-2-one (1.85 mg, 0.006 mmol) in *N,N*-dimethylformamide (DMF) solution (2 mL) at room temperature. The mixing solution turned to brown immediately and the filtrate was allowed to stand at room temperature for about 1 week. Several dark-brown block crystals were obtained. Elemental analysis – Anal. calcd. for $C_{60}H_{50}Co_2N_9O_{15}$ (%): C, 57.42; H, 4.02; N, 10.04. Found (%): C, 57.63; H, 4.15; N, 10.29.

Experimental details

The crystal structure was refined using the SHELX-14/7 package [2]. Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

Discussion

Co(II,III) complexes with organic ligands-containing nitrogen and oxygen donor atoms have been a hot topic in the field of coordination chemistry for many years [6–10]. Recently, many dinuclear cobalt(II,III) complexes have been studied concerning their preparation and their crystal structures [11–15]. In consideration of Schiff base and its derivatives, it can act as chelating ligand to form all kinds of stable transition metal complexes [16–18]. The Schiff bases Co(II,III) complexes exhibit a wide range of activities and applications, such as biochemistry [19], magnetic properties [20], photophysical properties [21] and so on.

X-ray crystallographic analysis of the title compound reveals an asymmetric binuclear structure, which consists of two Co(III) ions, three L^{2-} ligands, and three noncoordinated *N,N*-dimethylformamide (DMF) molecules. As shown in the figure, the Co1 center is coordinated in a O_3N_3 mode from the 2-(hydrazonomethyl)phenol ring of three L^{2-} ligands. Meanwhile, the Co2 center is coordinated also in a O_3N_3 manner, but from the coumarin ring in the same L^{2-} ligands. Thus, the coordination geometry of the Co(III) centers can be described as a slightly distorted octahedron, typical for this ligand [22, 23].

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