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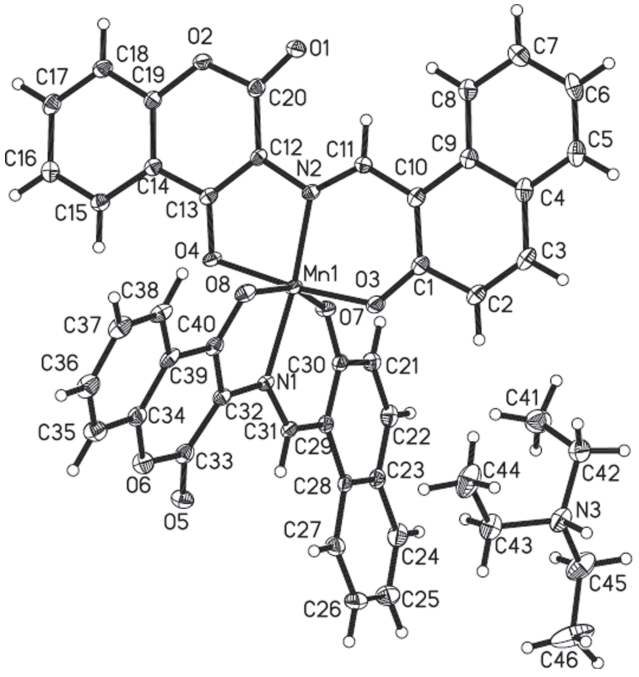
Crystal structure of triethylammonium bis{3-(((3-oxidonaphthalen-1-yl) methylene)amino)-2-oxo-2*H*-chromen-4-olato-κ³*O*,*N*,*O*′}manganese(III), $C_{46}H_{38}MnN_3O_8$



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Abstract

$C_{46}H_{38}MnN_3O_8$, triclinic $P\bar{1}$ (no. 2), $a = 8.9705(6)$ Å, $b = 12.0309(8)$ Å, $c = 18.4209(13)$ Å, $\alpha = 96.303(2)°$, $\beta = 103.884(2)°$, $\gamma = 101.636(2)°$, $Z = 2$, $V = 1864.0(2)$ Å^3, $R_{gt}(F) = 0.0496$, $wR_{ref}(F^2) = 0.1274$, $T = 296$ K.

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

Source of material

Synthesis of the ligand: The ligand was synthesized according to an analogous method reported previously in the literature [3, 4]. To an ethanol solution (5 mL) of 2-hydroxy-1-naphthaldehyde (172.2 mg, 1 mmol) was added an ethanol solution (5 mL) of 3-amino-4-hydroxy-2H-chromen-2-one (177.2 mg, 1 mmol). The solution was stirred under reflux conditions at 328 K for 8 h. After cooling to room temperature, the precipitate was filtered and washed with ethanol and hexane. The product was dried under vacuum and obtained orange-yellow solid (yield 78.7%, m.p. 554-555 K). Elemental analysis-Anal. calcd. for $C_{20}H_{13}NO_4$ (%): C, 72.50; H, 3.96; N, 4.23. Found (%): C, 76.47; H, 3.23; N, 4.85.

Synthesis of the manganese(III) complex: A methanol solution (4 mL) of manganese acetate tetrahydrate (12.3 mg, 0.05 mmol) was added dropwise to a mixed solution composed by triethylamine (0.5 mL) and orange yellow ethyl acetate solution (3.5 mL) of 4-hydroxy-3-[(2-hydroxy-naphthalen-1-ylmethylene)-amino]-chromen-2-one (33.1 mg, 0.1 mmol) at room temperature. The mixing solution turned to red-brown immediately and the filtrate was allowed to stand at room temperature for about three weeks. Dark reddish brown prismatical single were obtained. Elemental analysis-Anal. calcd. for $C_{46}H_{38}MnN_3O_8$ (%): C, 67.73; H, 4.70; N, 5.15. Found (%): C, 68.12; H, 4.55; N, 5.61.

Table 1: Data collection and handling.

Crystal:	Prismatical, dark reddish brown
Size:	0.17 × 0.15 × 0.08 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.42 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω-scans
$2\theta_{max}$, completeness:	50°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	12833, 6523, 0.033
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5038
$N(param)_{refined}$:	526
Programs:	Bruker programs [1], SHELX [2]

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

Discussion

Coumarin derivatives are well known to possess a diverse array of pharmacological and biochemical properties and has resulted in the chemistry of coumarins becoming well

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

Atom	x	y	z	U_{iso}*/U_{eq}
C1	0.4669(3)	0.4124(2)	0.23705(17)	0.0231(7)
C2	0.3454(4)	0.4191(3)	0.27364(18)	0.0286(7)
H2	0.3608	0.4811	0.3118	0.034*
C3	0.2078(4)	0.3375(3)	0.25426(18)	0.0295(7)
H3	0.1301	0.3455	0.2786	0.035*
C4	0.1797(4)	0.2399(3)	0.19753(18)	0.0283(7)
C5	0.0357(4)	0.1556(3)	0.1779(2)	0.0353(8)
H5	−0.0424	0.1646	0.2019	0.042*
C6	0.0099(4)	0.0606(3)	0.1241(2)	0.0404(9)
H6	−0.0856	0.0058	0.1114	0.048*
C7	0.1276(4)	0.0463(3)	0.0884(2)	0.0374(8)
H7	0.1110	−0.0192	0.0528	0.045*
C8	0.2674(4)	0.1283(3)	0.10543(18)	0.0300(7)
H8	0.3436	0.1177	0.0806	0.036*
C9	0.2982(3)	0.2284(2)	0.15997(17)	0.0235(7)
C10	0.4441(3)	0.3178(2)	0.17967(17)	0.0223(7)
C11	0.5565(3)	0.3090(2)	0.13771(16)	0.0197(6)
H11	0.5285	0.2479	0.0977	0.024*
C12	0.8060(3)	0.3636(2)	0.10817(16)	0.0197(6)
C13	0.9455(3)	0.4473(2)	0.13228(16)	0.0194(6)
C14	1.0656(3)	0.4444(2)	0.09275(16)	0.0208(6)
C15	1.2109(3)	0.5256(3)	0.11230(17)	0.0244(7)
H15	1.2354	0.5837	0.1539	0.029*
C16	1.3170(4)	0.5195(3)	0.07032(18)	0.0277(7)
H16	1.4131	0.5737	0.0834	0.033*
C17	1.2813(4)	0.4323(3)	0.00795(17)	0.0279(7)
H17	1.3532	0.4295	−0.0207	0.033*
C18	1.1410(4)	0.3506(3)	−0.01153(17)	0.0263(7)
H18	1.1177	0.2924	−0.0530	0.032*
C19	1.0348(3)	0.3562(2)	0.03159(17)	0.0221(7)
C20	0.7786(4)	0.2700(3)	0.04741(17)	0.0251(7)
C21	0.6400(3)	0.8090(3)	0.12853(18)	0.0269(7)
H21	0.6017	0.7714	0.0786	0.032*
C22	0.6246(4)	0.9168(3)	0.14491(19)	0.0289(7)
H22	0.5757	0.9518	0.1064	0.035*
C23	0.6827(3)	0.9790(3)	0.22116(19)	0.0265(7)
C24	0.6620(4)	1.0913(3)	0.2381(2)	0.0342(8)
H24	0.6117	1.1251	0.1992	0.041*
C25	0.7142(4)	1.1515(3)	0.3104(2)	0.0383(9)
H25	0.6992	1.2253	0.3207	0.046*
C26	0.7901(4)	1.1009(3)	0.3685(2)	0.0377(9)
H26	0.8260	1.1413	0.4178	0.045*
C27	0.8129(4)	0.9912(3)	0.35373(19)	0.0301(8)
H27	0.8640	0.9591	0.3934	0.036*
C28	0.7600(3)	0.9269(2)	0.27943(18)	0.0236(7)
C29	0.7761(3)	0.8087(2)	0.26148(17)	0.0221(7)
C30	0.7138(3)	0.7493(2)	0.18571(18)	0.0235(7)
C31	0.8644(3)	0.7608(2)	0.31898(17)	0.0211(6)
H31	0.9050	0.8076	0.3662	0.025*
C32	1.0061(3)	0.6304(2)	0.37516(16)	0.0217(7)
C33	1.1233(4)	0.7128(3)	0.43132(17)	0.0265(7)
C34	1.2151(4)	0.5608(3)	0.48944(18)	0.0280(7)
C35	1.3204(4)	0.5335(3)	0.55032(18)	0.0334(8)
H35	1.3925	0.5909	0.5873	0.040*
C36	1.3142(4)	0.4199(3)	0.5537(2)	0.0381(9)
H36	1.3817	0.3997	0.5942	0.046*
C37	1.2090(4)	0.3342(3)	0.49798(19)	0.0347(8)
H37	1.2076	0.2574	0.5012	0.042*
C38	1.1065(4)	0.3616(3)	0.43794(19)	0.0307(8)
H38	1.0362	0.3037	0.4007	0.037*
C39	1.1086(4)	0.4772(3)	0.43326(18)	0.0272(7)
C40	0.9981(4)	0.5108(3)	0.37218(17)	0.0240(7)
C41	0.2677(5)	0.8293(3)	0.1835(2)	0.0477(10)
H41A	0.2886	0.9089	0.1779	0.072*
H41B	0.2051	0.7830	0.1360	0.072*
H41C	0.3658	0.8067	0.1988	0.072*
C42	0.1800(4)	0.8125(3)	0.2423(2)	0.0435(9)
H42A	0.1707	0.7341	0.2520	0.052*
H42B	0.0740	0.8226	0.2226	0.052*
C43	0.4286(4)	0.8970(3)	0.3482(2)	0.0418(9)
H43A	0.4686	0.9468	0.3971	0.050*
H43B	0.4872	0.9294	0.3145	0.050*
C44	0.4577(5)	0.7782(3)	0.3573(3)	0.0578(12)
H44A	0.3974	0.7445	0.3893	0.087*
H44B	0.5681	0.7851	0.3798	0.087*
H44C	0.4259	0.7300	0.3085	0.087*
C45	0.2343(5)	1.0136(3)	0.3093(2)	0.0533(11)
H45A	0.1231	1.0083	0.2869	0.064*
H45B	0.2925	1.0450	0.2752	0.064*
C46	0.2879(7)	1.0942(4)	0.3841(3)	0.0824(17)
H46A	0.2565	1.0544	0.4224	0.124*
H46B	0.2406	1.1588	0.3795	0.124*
H46C	0.4009	1.1208	0.3981	0.124*
Mn1	0.78383(5)	0.52108(4)	0.22835(3)	0.02027(14)
N1	0.8969(3)	0.65847(19)	0.31452(13)	0.0198(5)
N2	0.6963(3)	0.37907(19)	0.15018(13)	0.0193(5)
N3	0.2583(3)	0.8950(2)	0.31728(17)	0.0377(7)
O1	0.6636(2)	0.18934(18)	0.02407(12)	0.0326(6)
O2	0.8964(2)	0.27109(17)	0.01051(11)	0.0256(5)
O3	0.5941(2)	0.49792(17)	0.25790(12)	0.0271(5)
O4	0.9674(2)	0.52927(16)	0.18929(11)	0.0223(5)
O5	1.1517(2)	0.81926(17)	0.43653(12)	0.0303(5)
H3A	0.2009	0.8677	0.3567	0.036*
O6	1.2245(3)	0.67639(18)	0.48821(12)	0.0308(5)
O7	0.7210(2)	0.64531(16)	0.16512(11)	0.0241(5)
O8	0.8983(2)	0.43668(17)	0.31846(11)	0.0264(5)

established. In particular, a series of coumarin-derived Schiff bases and their complexes were found to possess significant bioactivity [5]. Furthermore, Schiff base compounds are capable of forming all kinds of stable metal complexes [6–8], which are considered more and more important because their novelty structural, topological and widely using in the fields of biochemistry [9, 10], magnetic properties [11, 12], photophysical properties [13, 14], molecular recognition [15, 16] and so on.

The asymmetric unit of the title compound consists of a Mn(III) ion, two ligand units and a triethylammonium counter cation. The Mn(III) center is coordinated by a pair of N,O,O chelates from a pair of ligand units. The coordination

geometry of the Mn(III) center can be described as slightly distorted octahedron. Bond lengths and all other geometric parameters are in the expected ranges.

In the title crystal structure there is one classical charge-supported N—H···O hydrogen bond between the ammonium group and the O5 atom (N···O distance <2.8 Å).

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