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# Crystal structure of dimethanol-bis($\mu_2$-methanol-$\kappa^2O$:$O$)-bis{3-((4-methoxy-2-oxidobenzylidene)amino)-2-oxo-2$H$-chromen-4-olato-$\kappa^3O,N,O'$}dimanganese(II), $C_{38}H_{38}Mn_2N_2O_{14}$

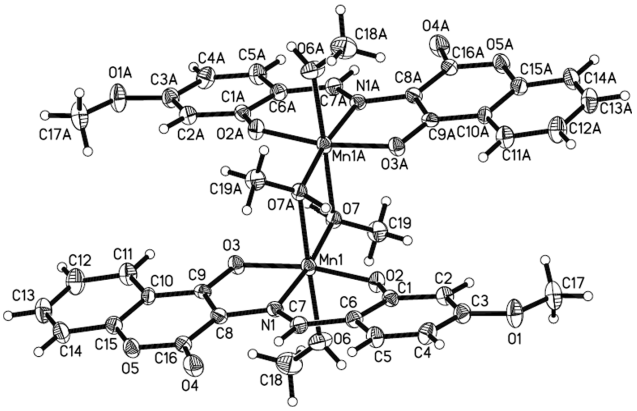


**Table 1:** Data collection and handling.

| | |
|---|---|
| Crystal: | Block, light-brown |
| Size: | 0.28 × 0.25 × 0.22 mm |
| Wavelength: | Mo $K\alpha$ radiation (0.71073 Å) |
| $\mu$: | 0.78 mm$^{-1}$ |
| Diffractometer, scan mode: | Bruker SMART, $\varphi$ and $\omega$-scans |
| $\theta_{max}$, completeness: | 26°, >99% |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$, $R_{int}$: | 5872, 3530, 0.048 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\ \sigma(I_{obs})$, 2422 |
| $N(param)_{refined}$: | 262 |
| Programs: | Bruker programs [1], SHELX [2] |

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## Abstract

$C_{38}H_{38}Mn_2N_2O_{14}$, triclinic, $P\bar{1}$ (no. 2), $a = 8.2828(12)$ Å, $b = 10.428(2)$ Å, $c = 12.152(3)$ Å, $\alpha = 113.44(2)°$, $\beta = 93.369(16)°$, $\gamma = 107.890(16)°$, $Z = 1$, $V = 896.5(3)$ Å$^3$, $R_{gt}(F) = 0.0578$, $wR_{ref}(F^2) = 0.1288$, $T = 293(2)$ 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:** All reagents and starting materials were obtained from commercial suppliers and used as received. The protonated form of the chromene-type ligand was synthesized according to an analogous method reported previously in the literature [3]. To an ethanol solution (5 mL) of 2-hydroxy-4-methoxybenzaldehyde (152.2 mg, 1 mmol) was added an ethanol solution (5 mL) of 3-amino-4-hydroxy-2$H$-chromen-2-one (177.2 mg, 1 mmol). The solution was stirred under reflux at 434 K for 6 h. After cooling to room temperature, the precipitate was filtered and washed with ethanol and hexane. The product (4-hydroxy-3-((2-hydroxy-4-methoxybenzylidene)amino)-2$H$-chromen-2-one) was dried under vacuum and obtained as a yellow solid (yield 71.8%, m.p. 460–461 K). Anal. calcd. for $C_{17}H_{13}NO_5$ (%): C, 65.59; H, 4.21; N, 4.50. Found (%): C, 66.47; H, 4.13; N, 4.85.

**Synthesis of the manganese(II) complex:** A methanol solution (4 mL) of manganese acetate tetrahydrate (12.3 mg, 0.05 mmol) was added dropwise to a solution of 4-hydroxy-3-((2-hydroxy-4-methoxybenzylidene)amino)-2$H$-chromen-2-one (6.0 mg, 20 mmol) in methanol (5 mL) at room temperature. The solution turned to brown immediately and the filtrate was allowed to stand at room temperature for about 2 weeks. Several light-brown block single-crystals were obtained. Anal. calcd. for $C_{38}H_{38}Mn_2N_2O_{14}$ (%): C, 53.28; H, 4.47; N, 3.27. Found (%): C, 55.12; H, 4.25; N, 3.61.

## 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 pharmacological and biochemical properties. Schiff base and its derivatives (contain −C=N− group) have been studied extensively and are known to coordinate with many metal ions through the azomethine nitrogen atom [4, 5]. And they can form all kinds of stable metal complexes [6, 7], which are considered to be more and more important, because of their biochemical [8, 9], magnetic [10, 11], photophysical [11, 12], and molecular

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

| Atom | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Mn1 | 0.05973(7) | 0.38312(6) | 0.52183(5) | 0.02963(17) |
| O1 | −0.3712(4) | 0.3542(3) | 0.9495(3) | 0.0550(9) |
| O2 | −0.0092(3) | 0.4163(3) | 0.6717(2) | 0.0353(7) |
| O3 | 0.1492(3) | 0.3246(2) | 0.3722(2) | 0.0340(6) |
| O4 | −0.1894(4) | −0.1680(3) | 0.2913(3) | 0.0482(8) |
| O5 | −0.0209(3) | −0.1284(3) | 0.1658(2) | 0.0394(7) |
| O6 | 0.3007(3) | 0.3707(3) | 0.6148(3) | 0.0492(8) |
| H6 | 0.289(2) | 0.344(3) | 0.6724(17) | 0.074* |
| O7 | 0.1609(3) | 0.5887(2) | 0.5641(2) | 0.0302(6) |
| N1 | −0.0660(4) | 0.1606(3) | 0.4555(3) | 0.0285(7) |
| C1 | −0.1377(4) | 0.3268(4) | 0.6954(3) | 0.0305(9) |
| C2 | −0.1874(4) | 0.3893(4) | 0.8081(3) | 0.0345(9) |
| H2 | −0.1314 | 0.4904 | 0.8608 | 0.041* |
| C3 | −0.3184(5) | 0.3013(4) | 0.8404(4) | 0.0398(10) |
| C4 | −0.4051(5) | 0.1503(4) | 0.7636(4) | 0.0422(11) |
| H4 | −0.4955 | 0.0928 | 0.7855 | 0.051* |
| C5 | −0.3566(5) | 0.0879(4) | 0.6569(4) | 0.0381(10) |
| H5 | −0.4123 | −0.0142 | 0.6073 | 0.046* |
| C6 | −0.2230(5) | 0.1723(4) | 0.6167(3) | 0.0332(9) |
| C7 | −0.1795(5) | 0.0972(4) | 0.5035(3) | 0.0342(9) |
| H7A | −0.2375 | −0.0058 | 0.4607 | 0.041* |
| C8 | −0.0194(4) | 0.0837(4) | 0.3417(3) | 0.0310(9) |
| C9 | 0.0964(4) | 0.1801(4) | 0.3061(3) | 0.0294(9) |
| C10 | 0.1598(4) | 0.1200(4) | 0.1963(3) | 0.0304(9) |
| C11 | 0.2781(5) | 0.2061(5) | 0.1537(4) | 0.0440(11) |
| H11 | 0.3194 | 0.3101 | 0.1962 | 0.053* |
| C12 | 0.3350(5) | 0.1391(5) | 0.0491(4) | 0.0526(13) |
| H12 | 0.4152 | 0.1972 | 0.0212 | 0.063* |
| C13 | 0.2727(5) | −0.0137(5) | −0.0134(4) | 0.0516(12) |
| H13 | 0.3125 | −0.0581 | −0.0837 | 0.062* |
| C14 | 0.1537(5) | −0.1038(5) | 0.0235(4) | 0.0477(12) |
| H14 | 0.1123 | −0.2076 | −0.0210 | 0.057* |
| C15 | 0.0971(5) | −0.0365(4) | 0.1286(4) | 0.0371(10) |
| C16 | −0.0835(5) | −0.0740(4) | 0.2703(3) | 0.0335(9) |
| C17 | −0.2836(6) | 0.5068(5) | 1.0355(4) | 0.0605(15) |
| H17A | −0.2901 | 0.5708 | 0.9977 | 0.091* |
| H17B | −0.1642 | 0.5235 | 1.0616 | 0.091* |
| H17C | −0.3374 | 0.5290 | 1.1053 | 0.091* |
| C18 | 0.4554(6) | 0.3601(5) | 0.5764(5) | 0.0628(14) |
| H18A | 0.4336 | 0.3118 | 0.4884 | 0.094* |
| H18B | 0.4962 | 0.3025 | 0.6084 | 0.094* |
| H18C | 0.5416 | 0.4588 | 0.6061 | 0.094* |
| C19 | 0.2679(5) | 0.6924(4) | 0.6791(4) | 0.0483(12) |
| H19A | 0.2075 | 0.6846 | 0.7426 | 0.072* |
| H19B | 0.2976 | 0.7920 | 0.6855 | 0.072* |
| H19C | 0.3718 | 0.6715 | 0.6880 | 0.072* |
| H7 | 0.191(4) | 0.601(3) | 0.5012(17) | 0.058* |

recognition [14] properties. So, a series of coumarin-derived Schiff bases and their complexes have a significant position in the field of coordination chemistry.

The title complex is a dinuclear complex, which consists of two Mn(II) ions, two tridentate ligands, two $\mu_2$-bridging methanol molecules and two coordinated methanol molecules. As shown in the figure, each Mn(II) center is coordinated by one N and two O atoms from a tridentate chromene ligand, and one methanol molecule to obtain two [MnL(MeOH)] moieties. [MnL(MeOH)] moieties are bridged via two methanol molecules to form the dinuclear title complex. The coordination geometry of the Mn(II) center can be described as a slightly distorted octahedron.

In the crystal structure intramolecular O—H···O hydrogen bonds link the title complex to a supramolecular structure. This linkage is further stabilized by three π···π stacking interactions with centroid-centroid distances of 3.659(2)–3.931(3) Å.

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