Crystal structure of [bis-tris(pyrazolyl)methanecopper(II)] [chloro-bis(η^2 -benzoato)- η^1 -benzoato-manganate(II)] hydrate, $\text{Cu}(\text{C}_{10}\text{H}_{10}\text{N}_6)\text{Mn}(\text{C}_7\text{H}_5\text{O}_2)_3\text{Cl} \cdot \text{H}_2\text{O}$

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Received May 15, 2003, accepted and available on-line August 21, 2003; CCDC-No. 1267/1091

Abstract

$\text{C}_{41}\text{H}_{37}\text{ClCuMnN}_{12}\text{O}_7$, monoclinic, $P12_1/n1$ (No. 14), $a = 15.946(3) \text{ \AA}$, $b = 13.26(2) \text{ \AA}$, $c = 20.766(5) \text{ \AA}$, $\beta = 106.49(2)^\circ$, $V = 4209.3 \text{ \AA}^3$, $Z = 4$, $R_{\text{gt}}(F) = 0.060$, $wR_{\text{ref}}(F^2) = 0.155$, $T = 293 \text{ K}$.

Source of material

The blue title compound, $[\text{Cu}^{\text{II}}(\text{pz}_3\text{CH})_2][\text{Mn}^{\text{II}}(\text{O}_2\text{CPh})_3(\text{Cl})] \cdot \text{H}_2\text{O}$, was obtained during attempts to make a benzoate bridged heterotrimetallic MnCuMn complex by reacting $(\text{pz}_3\text{CH})\text{Mn}(\text{Cl})_2$ with CuCl_2 and sodium benzoate in methanol-water solution, in 2:1 Mn:Cu ratio. Ligand transfer to Cu(II) occurred with subsequent formation of the $[(\text{pz}_3\text{CH})_2\text{Cu}]_2^+$ cation. The complex was characterized by IR spectroscopy which showed the $\nu(\text{asymm})$ OCO frequencies of the benzoate groups at 1594 cm^{-1} and the characteristic pz_3CH bands.

Experimental details

The C-bound H atoms were placed in their geometrically calculated positions and included in the final refinement in the riding model approximation. The water-bound H atoms were located from a difference map but were not refined.

Discussion

The structure comprises $[\text{Mn}^{\text{II}}(\text{O}_2\text{CPh})_3(\text{Cl})]$ anions, $[\text{Cu}^{\text{II}}(\text{pz}_3\text{CH})_2]$ cations and a solvent water molecule in the ratio 1:2:1 as the cations are each disposed about a centre of inversion. For the cations, the coordination geometry is tetragonally distorted octahedral with the range of $d(\text{Cu}-\text{N})$ being $1.990(5) \text{ \AA}$ to $2.374(6) \text{ \AA}$. In the anion, the manganese centre is also distorted octahedral but the geometry is defined by a chloride and five oxygens, the latter derived from two chelating and one monodentate benzoate ligands. The $d(\text{Mn}-\text{O})$ distances for the bidentate ligands lie in the range $2.190(6) \text{ \AA}$ to $2.299(6) \text{ \AA}$ and $d(\text{Mn}-\text{O}71)$ is shorter at $2.075(6) \text{ \AA}$. In terms of angles, the greatest deviation from the ideal octahedral geometry is found in the $\angle \text{O}91-\text{Mn}-\text{O}92$ chelate angle of $56.7(2)^\circ$. The solvent water molecule straddles the anion in that it forms hydrogen bonds to both the O72 and O81 atoms so that $d(\text{O}1-\text{H}\cdots\text{O}72) = 1.80 \text{ \AA}$, $d(\text{O}1\cdots\text{O}72) = 2.868(8) \text{ \AA}$ and angle at H of 163° , and $d(\text{O}1-\text{H}\cdots\text{O}81) = 2.01 \text{ \AA}$, $d(\text{O}1\cdots\text{O}81) = 3.035(9) \text{ \AA}$ and the angle at H of 171° . The structure is isomorphous with the cobalt(II) analogue [1]. The various binding modes of carboxylate ligands in bio-related studies of iron and manganese proteins has been emphasised by Lippard [2]. In the present anionic Mn(II) moiety, the combination of bidentate and unidentate benzoate ligands is therefore of interest.

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Table 1. Data collection and handling.

Crystal:	blue block, size 0.16 × 0.24 × 0.24 mm
Wavelength:	Mo K α radiation (0.7107 Å)
μ :	9.35 cm ⁻¹
Diffractometer, scan mode:	Rigaku AFC6R, $\omega/2\theta$
$2\theta_{\max}$:	50.2°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	8125, 7475
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3177
$N(\text{param})_{\text{refined}}$:	572
Programs:	teXsan [3], SHELXS-86 [4], SHELXL-97 [5], DIFABS [6], PLATON [7], ORTEPII [8]

Table 2. Continued.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(22)	4e	0.1127	0.1745	0.1377	0.068
H(23)	4e	0.2316	0.2984	0.1639	0.068
H(31)	4e	-0.0005	0.6827	0.1353	0.068
H(32)	4e	0.1287	0.7139	0.2271	0.068
H(33)	4e	0.2457	0.6049	0.2089	0.068
H(41)	4e	0.1990	0.5791	-0.4174	0.068
H(42)	4e	0.2985	0.4779	-0.3265	0.068
H(43)	4e	0.2146	0.3266	-0.3127	0.068
H(51)	4e	-0.1768	0.5216	-0.4433	0.068
H(52)	4e	-0.1974	0.4119	-0.3524	0.068
H(53)	4e	-0.0754	0.2891	-0.3268	0.068
H(61)	4e	-0.0040	0.2773	-0.6173	0.068
H(62)	4e	0.0235	0.1052	-0.5731	0.068
H(63)	4e	0.0505	0.1145	-0.4509	0.068
H(73)	4e	0.0926	0.1399	-0.0970	0.068
H(74)	4e	0.1833	0.1773	0.0084	0.068
H(75)	4e	0.3014	0.2803	0.0203	0.068
H(76)	4e	0.3313	0.3489	-0.0728	0.068
H(77)	4e	0.2427	0.3104	-0.1786	0.068
H(83)	4e	0.1460	-0.2308	-0.2462	0.068
H(84)	4e	0.1885	-0.3967	-0.2468	0.068
H(85)	4e	0.0907	-0.5254	-0.2512	0.068
H(86)	4e	-0.0488	-0.4887	-0.2538	0.068
H(87)	4e	-0.0950	-0.3250	-0.2561	0.068
H(93)	4e	-0.0785	0.0194	-0.0302	0.068
H(94)	4e	-0.1197	0.0808	0.0599	0.068
H(95)	4e	-0.2267	0.2052	0.0403	0.068
H(96)	4e	-0.2964	0.2552	-0.0659	0.068
H(97)	4	-0.2544	0.1902	-0.1556	0.068

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(1o)	4e	0.1023	-0.0090	-0.3099	0.085
H(2o)	4e	0.1225	0.0978	-0.3148	0.085
H(1)	4e	0.2529	0.4758	0.1194	0.085
H(2)	4e	0.0595	0.2605	-0.3679	0.085
H(11)	4e	0.0917	0.5715	-0.1169	0.068
H(12)	4e	0.2510	0.5751	-0.0967	0.068
H(13)	4e	0.3157	0.5259	0.0229	0.068
H(21)	4e	-0.0093	0.2506	0.0478	0.068

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Cu(1)	2c	0	1/2	0	0.0384(7)	0.0580(9)	0.0491(7)	0.0014(7)	0.0151(6)	0.0010(7)
Cu(2)	2d	0	1/2	1/2	0.0431(7)	0.0386(7)	0.0349(6)	-0.0006(6)	0.0098(5)	0.0107(6)
Mn	4e	-0.05038(7)	0.03382(8)	-0.25049(5)	0.0505(7)	0.0510(8)	0.0587(7)	-0.0060(6)	0.0139(6)	0.0012(6)
Cl(1)	4e	-0.0955(1)	0.0812(2)	-0.36772(9)	0.063(1)	0.063(1)	0.059(1)	-0.008(1)	0.005(1)	0.001(1)
O(1)	4e	0.1393(3)	0.0271(4)	-0.3362(3)	0.084(4)	0.106(5)	0.091(4)	-0.007(4)	0.052(3)	-0.015(3)
O(71)	4e	0.0287(4)	0.1594(4)	-0.2203(3)	0.066(4)	0.083(4)	0.087(4)	-0.028(3)	0.022(3)	-0.031(3)
O(72)	4e	0.1289(3)	0.2116(4)	-0.2668(2)	0.096(4)	0.070(4)	0.037(3)	-0.014(3)	0.012(3)	0.009(3)
O(81)	4e	0.0470(3)	-0.0837(4)	-0.2480(3)	0.074(4)	0.054(4)	0.085(4)	-0.011(3)	0.022(3)	0.001(3)
O(82)	4e	-0.0883(3)	-0.1336(4)	-0.2655(2)	0.059(4)	0.062(4)	0.083(4)	0.010(3)	0.016(3)	0.011(3)
O(91)	4e	-0.0604(4)	0.0139(5)	-0.1446(3)	0.100(5)	0.083(5)	0.114(5)	0.020(4)	0.069(4)	0.014(4)
O(92)	4e	-0.1683(4)	0.0863(4)	-0.2170(3)	0.103(5)	0.074(4)	0.084(4)	-0.009(4)	0.038(4)	-0.015(4)
N(11)	4e	0.1114(3)	0.5285(4)	-0.0218(3)	0.037(3)	0.065(4)	0.045(3)	0.002(3)	0.012(3)	-0.004(3)
N(12)	4e	0.1890(3)	0.5134(4)	0.0263(2)	0.042(3)	0.042(4)	0.048(3)	0.000(3)	0.019(3)	0.006(3)
N(21)	4e	0.0661(4)	0.3732(5)	0.0534(3)	0.054(4)	0.063(5)	0.065(4)	-0.017(4)	0.018(4)	-0.003(4)
N(22)	4e	0.1494(4)	0.3859(4)	0.0927(3)	0.049(4)	0.046(4)	0.047(4)	0.003(3)	0.016(3)	0.002(3)
N(31)	4e	0.0662(4)	0.5805(5)	0.0976(3)	0.053(4)	0.064(5)	0.068(4)	0.024(4)	0.027(4)	0.006(4)
N(32)	4e	0.1514(4)	0.5559(4)	0.1246(3)	0.042(4)	0.058(4)	0.048(4)	0.010(3)	0.010(3)	-0.001(3)
N(41)	4e	0.1086(3)	0.4707(4)	-0.4256(2)	0.040(3)	0.030(3)	0.038(3)	-0.004(3)	0.005(2)	0.010(2)
N(42)	4e	0.1154(3)	0.3849(4)	-0.3890(2)	0.044(3)	0.034(3)	0.034(3)	0.001(3)	0.009(3)	0.006(3)
N(51)	4e	-0.0672(3)	0.4437(4)	-0.4383(2)	0.049(4)	0.036(3)	0.039(3)	0.003(3)	0.015(3)	0.011(3)
N(52)	4e	-0.0340(3)	0.3633(4)	-0.3987(2)	0.043(3)	0.030(3)	0.032(3)	-0.001(3)	0.012(3)	0.005(2)
N(61)	4e	0.0147(4)	0.3264(4)	-0.5227(3)	0.062(4)	0.042(4)	0.039(3)	0.008(3)	0.015(3)	0.007(3)
N(62)	4e	0.0315(3)	0.2668(4)	-0.4669(2)	0.054(4)	0.026(3)	0.036(3)	-0.002(3)	0.015(3)	0.003(3)
C(1)	4e	0.1915(4)	0.4824(5)	0.0931(3)	0.036(4)	0.045(5)	0.045(4)	0.000(4)	0.008(3)	0.002(4)
C(2)	4e	0.0449(4)	0.3132(5)	-0.4024(3)	0.040(4)	0.034(4)	0.036(4)	0.003(3)	0.010(3)	0.005(3)
C(11)	4e	0.1323(5)	0.5558(5)	-0.0762(3)	0.052(5)	0.072(6)	0.046(4)	-0.002(4)	0.024(4)	0.009(4)
C(12)	4e	0.2211(5)	0.5584(5)	-0.0657(4)	0.053(5)	0.070(6)	0.058(5)	0.001(4)	0.030(4)	0.006(4)
C(13)	4e	0.2565(4)	0.5312(5)	0.0003(3)	0.040(4)	0.049(5)	0.069(5)	-0.003(4)	0.026(4)	-0.008(4)
C(21)	4e	0.0440(6)	0.2816(7)	0.0680(4)	0.066(6)	0.082(7)	0.082(7)	-0.027(6)	0.039(5)	-0.026(6)
C(22)	4e	0.1125(7)	0.2377(6)	0.1182(5)	0.109(8)	0.045(6)	0.090(7)	-0.005(6)	0.065(6)	-0.002(5)
C(23)	4e	0.1773(5)	0.3055(6)	0.1324(4)	0.072(6)	0.054(5)	0.051(5)	0.013(5)	0.027(4)	0.009(4)
C(31)	4e	0.0528(6)	0.6505(6)	0.1406(4)	0.072(6)	0.068(6)	0.083(6)	0.031(5)	0.046(6)	0.024(5)
C(32)	4e	0.1241(6)	0.6690(6)	0.1918(4)	0.103(8)	0.047(5)	0.065(6)	0.009(5)	0.038(6)	0.013(4)

Table 3. Continued.

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
C(33)	4e	0.1882(5)	0.6090(5)	0.1820(4)	0.060(5)	0.047(5)	0.056(5)	−0.001(4)	0.016(4)	0.008(4)
C(41)	4e	0.1850(5)	0.5174(5)	−0.4019(3)	0.056(5)	0.043(5)	0.047(4)	−0.008(4)	0.016(4)	0.004(4)
C(42)	4e	0.2414(5)	0.4617(6)	−0.3506(3)	0.044(4)	0.068(6)	0.048(4)	−0.009(4)	0.003(3)	0.003(4)
C(43)	4e	0.1951(4)	0.3786(6)	−0.3434(3)	0.041(4)	0.061(5)	0.033(4)	0.008(4)	0.002(3)	0.008(4)
C(51)	4e	−0.1396(4)	0.4695(5)	−0.4229(3)	0.042(4)	0.056(5)	0.048(4)	0.007(4)	0.011(3)	0.000(4)
C(52)	4e	−0.1522(4)	0.4081(5)	−0.3725(3)	0.049(4)	0.056(5)	0.053(4)	0.001(4)	0.026(4)	−0.001(4)
C(53)	4e	−0.0848(4)	0.3408(5)	−0.3583(3)	0.058(5)	0.039(4)	0.041(4)	−0.018(4)	0.021(4)	−0.001(3)
C(61)	4e	0.0087(4)	0.2602(6)	−0.5721(4)	0.049(5)	0.073(6)	0.047(4)	−0.003(4)	0.014(4)	−0.003(4)
C(62)	4e	0.0236(5)	0.1632(6)	−0.5478(4)	0.058(5)	0.061(6)	0.063(5)	0.010(5)	0.013(4)	−0.025(5)
C(63)	4e	0.0383(4)	0.1679(5)	−0.4811(3)	0.048(4)	0.042(5)	0.045(4)	0.000(4)	0.003(3)	−0.004(4)
C(71)	4e	0.1020(5)	0.1958(5)	−0.2179(4)	0.055(5)	0.032(4)	0.056(5)	0.001(4)	0.020(4)	−0.006(4)
C(72)	4e	0.1588(4)	0.2215(5)	−0.1489(3)	0.047(4)	0.031(4)	0.042(4)	0.010(4)	0.018(3)	0.001(3)
C(73)	4e	0.1408(5)	0.1816(5)	−0.0924(3)	0.053(5)	0.048(5)	0.046(4)	0.016(4)	0.019(4)	0.004(4)
C(74)	4e	0.1950(6)	0.2043(6)	−0.0295(4)	0.099(7)	0.069(6)	0.043(5)	0.037(6)	0.025(5)	−0.001(4)
C(75)	4e	0.2653(6)	0.2657(7)	−0.0224(4)	0.077(7)	0.071(7)	0.061(6)	0.030(6)	−0.015(5)	−0.026(5)
C(76)	4e	0.2835(5)	0.3064(6)	−0.0778(4)	0.049(5)	0.063(6)	0.083(6)	−0.001(4)	−0.002(5)	−0.016(5)
C(77)	4e	0.2303(5)	0.2836(5)	−0.1409(3)	0.052(5)	0.045(5)	0.057(5)	0.000(4)	0.014(4)	−0.010(4)
C(81)	4e	−0.0092(6)	−0.1529(6)	−0.2561(3)	0.058(5)	0.053(5)	0.049(5)	−0.005(5)	0.013(4)	0.013(4)
C(82)	4e	0.0206(5)	−0.2606(6)	−0.2521(3)	0.046(5)	0.049(5)	0.039(4)	−0.003(4)	0.009(4)	0.002(4)
C(83)	4e	0.1058(5)	−0.2824(7)	−0.2486(3)	0.065(6)	0.067(6)	0.057(5)	−0.001(5)	0.015(4)	−0.012(4)
C(84)	4e	0.1310(7)	−0.3816(9)	−0.2485(4)	0.082(7)	0.13(1)	0.051(5)	0.046(7)	0.016(5)	−0.010(6)
C(85)	4e	0.073(1)	−0.4586(9)	−0.2510(4)	0.18(1)	0.068(7)	0.060(6)	0.029(9)	0.030(8)	−0.009(5)
C(86)	4e	−0.0094(7)	−0.4366(7)	−0.2531(4)	0.113(9)	0.058(7)	0.055(5)	−0.021(6)	0.016(6)	−0.013(5)
C(87)	4e	−0.0371(5)	−0.3388(6)	−0.2541(3)	0.069(5)	0.053(5)	0.046(4)	0.004(5)	0.019(4)	−0.003(4)
C(91)	4e	−0.1299(7)	0.0640(6)	−0.1583(5)	0.090(8)	0.048(6)	0.091(7)	−0.016(5)	0.049(7)	−0.003(5)
C(92)	4e	−0.1619(6)	0.0999(6)	−0.1015(4)	0.070(6)	0.052(6)	0.077(6)	−0.019(5)	0.045(5)	−0.011(5)
C(93)	4e	−0.1225(5)	0.0676(6)	−0.0373(5)	0.070(6)	0.068(6)	0.094(7)	−0.022(5)	0.033(6)	−0.010(6)
C(94)	4e	−0.1462(8)	0.1040(9)	0.0166(5)	0.14(1)	0.11(1)	0.075(7)	−0.057(8)	0.049(7)	−0.021(7)
C(95)	4e	−0.211(1)	0.177(1)	0.0044(7)	0.17(1)	0.10(1)	0.15(1)	−0.08(1)	0.12(1)	−0.08(1)
C(96)	4e	−0.2516(8)	0.2078(7)	−0.0584(7)	0.12(1)	0.055(7)	0.18(1)	−0.020(6)	0.10(1)	−0.023(8)
C(97)	4e	−0.2265(6)	0.1688(7)	−0.1121(5)	0.092(7)	0.057(6)	0.109(8)	−0.023(5)	0.060(6)	−0.003(5)

Acknowledgment. The Australian Research Council is thanked for support.

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