Crystal structure of [bis-tris(pyrazolyl)methanecopper(II)] [chloro-bis(η^2-benzoato)-η^1-benzoato-manganate(II)] hydrate, $Cu(C_{10}H_{10}N_6)Mn(C_7H_5O_2)_3Cl \cdot H_2O$

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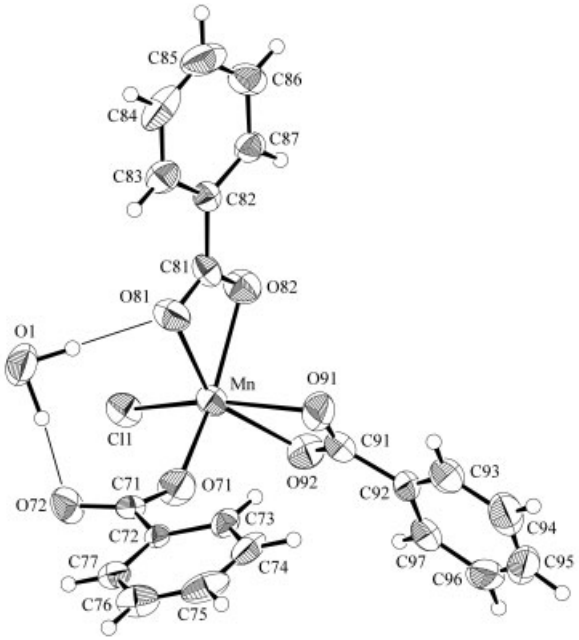

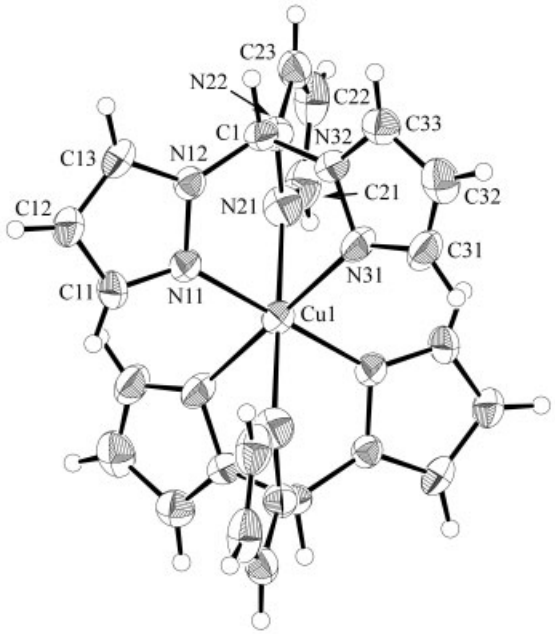

Abstract

$C_{41}H_{37}ClCuMnN_{12}O_7$, monoclinic, $P12_1/n1$ (No. 14), $a = 15.946(3)$ Å, $b = 13.26(2)$ Å, $c = 20.766(5)$ Å, $\beta = 106.49(2)°$, $V = 4209.3$ Å^3, $Z = 4$, $R_{gt}(F) = 0.060$, $wR_{ref}(F^2) = 0.155$, $T = 293$ K.

Source of material

The blue title compound, $[Cu^{II}(pz_3CH)_2][Mn^{II}(O_2CPh)_3(Cl)] \cdot H_2O$, was obtained during attempts to make a benzoate bridged heterotrimetallic MnCuMn complex by reacting $(pz_3CH)Mn(Cl)_2$ 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 $[(pz_3CH)_2Cu]_2^+$ cation. The complex was characterized by IR spectroscopy which showed the ν(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 $[Mn^{II}(O_2CPh)_3(Cl)]$ anions, $[Cu^{II}(pz_3CH)_2]$ 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(Cu—N) being 1.990(5) Å to 2.374(6) Å. 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(Mn—O) distances for the bidentate ligands lie in the range 2.190(6) Å to 2.299(6) Å and d(Mn—O71) is shorter at 2.075(6) Å. In terms of angles, the greatest deviation from the ideal octahedral geometry is found in the ∠O91–Mn-–O92 chelate angle of 56.7(2)°. The solvent water molecule straddles the anion in that it forms hydrogen bonds to both the O72 and O81 atoms so that d(O1–H···O72) = 1.80 Å, d(O1···O72) = 2.868(8) Å and angle at H of 163°, and d(O1–H···O81) = 2.01 Å, d(O1···O81) = 3.035(9) Å 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°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8125, 7475
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3177
$N(param)_{refined}$:	572
Programs:	teXsan [3], SHELXS-86 [4], SHELXL-97 [5], DIFABS [6], PLATON [7], ORTEPII [8]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1o)	4*e*	0.1023	–0.0090	–0.3099	0.085
H(2o)	4*e*	0.1225	0.0978	–0.3148	0.085
H(1)	4*e*	0.2529	0.4758	0.1194	0.085
H(2)	4*e*	0.0595	0.2605	–0.3679	0.085
H(11)	4*e*	0.0917	0.5715	–0.1169	0.068
H(12)	4*e*	0.2510	0.5751	–0.0967	0.068
H(13)	4*e*	0.3157	0.5259	0.0229	0.068
H(21)	4*e*	–0.0093	0.2506	0.0478	0.068
H(22)	4*e*	0.1127	0.1745	0.1377	0.068
H(23)	4*e*	0.2316	0.2984	0.1639	0.068
H(31)	4*e*	–0.0005	0.6827	0.1353	0.068
H(32)	4*e*	0.1287	0.7139	0.2271	0.068
H(33)	4*e*	0.2457	0.6049	0.2089	0.068
H(41)	4*e*	0.1990	0.5791	–0.4174	0.068
H(42)	4*e*	0.2985	0.4779	–0.3265	0.068
H(43)	4*e*	0.2146	0.3266	–0.3127	0.068
H(51)	4*e*	–0.1768	0.5216	–0.4433	0.068
H(52)	4*e*	–0.1974	0.4119	–0.3524	0.068
H(53)	4*e*	–0.0754	0.2891	–0.3268	0.068
H(61)	4*e*	–0.0040	0.2773	–0.6173	0.068
H(62)	4*e*	0.0235	0.1052	–0.5731	0.068
H(63)	4*e*	0.0505	0.1145	–0.4509	0.068
H(73)	4*e*	0.0926	0.1399	–0.0970	0.068
H(74)	4*e*	0.1833	0.1773	0.0084	0.068
H(75)	4*e*	0.3014	0.2803	0.0203	0.068
H(76)	4*e*	0.3313	0.3489	–0.0728	0.068
H(77)	4*e*	0.2427	0.3104	–0.1786	0.068
H(83)	4*e*	0.1460	–0.2308	–0.2462	0.068
H(84)	4*e*	0.1885	–0.3967	–0.2468	0.068
H(85)	4*e*	0.0907	–0.5254	–0.2512	0.068
H(86)	4*e*	–0.0488	–0.4887	–0.2538	0.068
H(87)	4*e*	–0.0950	–0.3250	–0.2561	0.068
H(93)	4*e*	–0.0785	0.0194	–0.0302	0.068
H(94)	4*e*	–0.1197	0.0808	0.0599	0.068
H(95)	4*e*	–0.2267	0.2052	0.0403	0.068
H(96)	4*e*	–0.2964	0.2552	–0.0659	0.068
H(97)	4	–0.2544	0.1902	–0.1556	0.068

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	2*c*	0	1/2	0	0.0384(7)	0.0580(9)	0.0491(7)	0.0014(7)	0.0151(6)	0.0010(7)
Cu(2)	2*d*	0	1/2	1/2	0.0431(7)	0.0386(7)	0.0349(6)	–0.0006(6)	0.0098(5)	0.0107(6)
Mn	4*e*	–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)	4*e*	–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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	–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)	4*e*	–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)	4*e*	–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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	–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)	4*e*	–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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	–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)	4*e*	–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)	4*e*	–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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	–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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	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)	4*e*	–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)	4*e*	–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)	4*e*	–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)	4*e*	–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)	4*e*	–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)	4*e*	–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)	4*e*	–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)	4*e*	–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)	4*e*	–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)

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