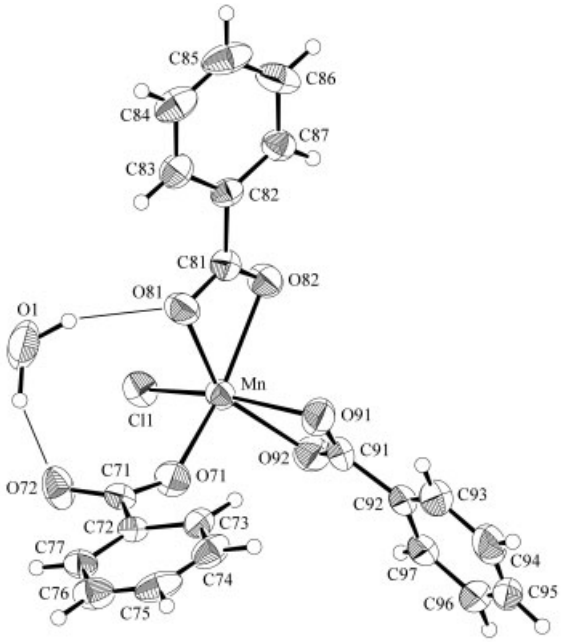
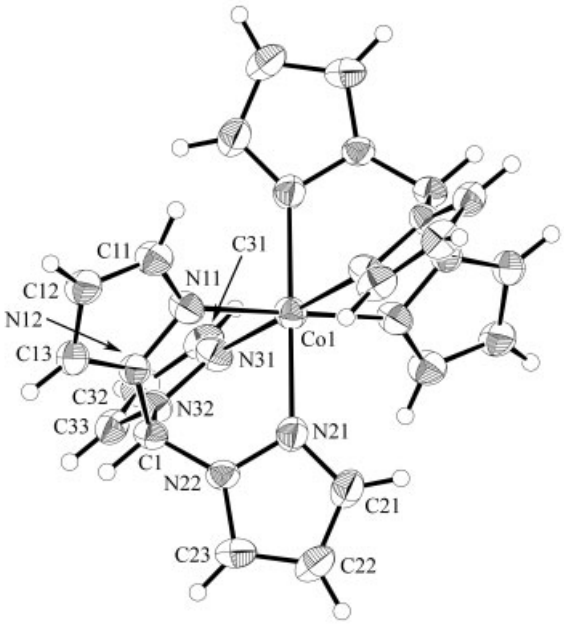
Crystal structure of [bis-tris(pyrazolyl)methanecobalt(II)] [chloro-bis(η^2-benzoato)-η^1-benzoato-manganate(II)] hydrate, $Co(C_{10}H_{10}N_6)Mn(C_7H_5O_2)_3Cl \cdot H_2O$

B. Moubaraki[I], K. S. Murray[I] and E. R. T. Tiekink*[,II,1]

[I] Monash University, School of Chemistry, PO Box 23, Clayton, Victoria 3800, Australia
[II] The University of Adelaide, Department of Chemistry, Australia 5005

Received May 15, 2003, accepted and available on-line August 21, 2003; CCDC-No. 1267/1092





Abstract

$C_{41}H_{37}ClCoMnN_{12}O_7$, monoclinic, $P12_1/n1$ (No. 14), $a = 16.024(5)$ Å, $b = 13.23(1)$ Å, $c = 20.833(4)$ Å, $\beta = 106.54(2)°$, $V = 4233.8$ Å^3, $Z = 4$, $R_{gt}(F) = 0.054$, $wR_{ref}(F^2) = 0.138$, $T = 293$ K.

Source of material

The blue title compound, $[Co^{II}(pz_3CH)_2][Mn^{II}(O_2CPh)_3(Cl)] \cdot H_2O$, was obtained during attempts to make a benzoate bridged heterotrimetallic MnCoMn complex by reacting $(pz_3CH)Mn(Cl)_2$ with $CoCl_2$ and sodium benzoate in methanol-water solution, in 2:1 Mn:Co ratio. Ligand transfer to Co(II) occurred with subsequent formation of the $[(pz_3CH)_2Co]^{2+}$ 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 is isomorphous with the copper(II) analogue [1] and comprises $[Mn^{II}(O_2CPh)_3(Cl)]$ anions, two centrosytmmetric $[Co^{II}(pz_3CH)_2]^{2+}$ cations and a solvent water molecule. For the cations, the cobalt atom exists in a tetragonally distorted octahedral geometry with the Co—N distances in the range 2.084(4) Å to 2.140(4) Å. A similar coordination polyhedron is found in the anion, but one defined by a chloride and five oxygens as there are two chelating and one monodentate benzoate ligands. The range of d(Mn—O) distances for the bidentate ligands is somewhat wider than for the copper analogue at 2.164(4) Å to 2.355(5) Å and d(Mn—O71) is shorter at 2.073(4) Å. The solvent water molecule is associated with the anion via two hydrogen bonds with d(O1–H···O72) = 1.86 Å, d(O1···O72) = 2.861(7) Å and angle at H of 153°, and d(O1–H···O81) = 2.19 Å, d(O1···O81) = 3.149(7) Å with the angle at H of 155°. As emphasised by Lippard [2], various binding modes of carboxylate ligands in iron and manganese proteins are known.

* Correspondence author (e-mail: chmtert@nus.edu.sg)
[1] Current address: The National University of Singapore, Department of Chemistry, Singapore 117543

Table 1. Data collection and handling.

Crystal:	purple octahedron, size 0.16 × 0.16 × 0.24 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	8.19 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC6R, $\omega/2\theta$
$2\theta_{max}$:	50.2°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8162, 7509
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3674
$N(param)_{refined}$:	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(1w)	4*e*	0.1437	0.1113	–0.3204	0.075
H(2w)	4*e*	0.1165	–0.0180	–0.3132	0.075
H(1)	4*e*	0.2541	0.4765	0.1166	0.075
H(2)	4*e*	0.0577	0.2584	–0.3695	0.075
H(11)	4*e*	0.0963	0.5778	–0.1188	0.075
H(12)	4*e*	0.2558	0.5806	–0.0971	0.075
H(13)	4*e*	0.3180	0.5276	0.0211	0.075
H(21)	4*e*	–0.0071	0.2509	0.0497	0.075
H(22)	4*e*	0.1137	0.1752	0.1378	0.075
H(23)	4*e*	0.2342	0.2989	0.1609	0.075
H(31)	4*e*	–0.0103	0.6738	0.1244	0.075
H(32)	4*e*	0.1197	0.7137	0.2199	0.075
H(33)	4*e*	0.2397	0.6080	0.2036	0.075
H(41)	4*e*	0.2073	0.5743	–0.4115	0.075
H(42)	4*e*	0.3029	0.4673	–0.3234	0.075
H(43)	4*e*	0.2149	0.3171	–0.3132	0.075
H(51)	4*e*	–0.1762	0.5195	–0.4350	0.075
H(52)	4*e*	–0.1953	0.4040	–0.3461	0.075
H(53)	4*e*	–0.0695	0.2852	–0.3218	0.075
H(61)	4*e*	–0.0069	0.3099	–0.6173	0.075
H(62)	4*e*	0.0212	0.1303	–0.5848	0.075
H(63)	4*e*	0.0482	0.1238	–0.4611	0.075
H(73)	4*e*	0.0908	0.1377	–0.0958	0.075
H(74)	4*e*	0.1843	0.1704	0.0095	0.075
H(75)	4*e*	0.3014	0.2744	0.0213	0.075
H(76)	4*e*	0.3292	0.3453	–0.0710	0.075
H(77)	4*e*	0.2404	0.3090	–0.1770	0.075
H(83)	4*e*	0.1435	–0.2263	–0.2522	0.075
H(84)	4*e*	0.1952	–0.3890	–0.2485	0.075
H(85)	4*e*	0.1019	–0.5221	–0.2513	0.075
H(86)	4*e*	–0.0385	–0.4943	–0.2518	0.075
H(87)	4*e*	–0.0922	–0.3309	–0.2566	0.075
H(93)	4*e*	–0.0809	0.0223	–0.0323	0.075
H(94)	4*e*	–0.1269	0.0860	0.0552	0.075
H(95)	4*e*	–0.2330	0.2076	0.0350	0.075
H(96)	4*e*	–0.3009	0.2567	–0.0719	0.075
H(97)	4*e*	–0.2578	0.1923	–0.1600	0.075

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}
Co(1)	2*c*	0	1/2	0	0.0402(6)	0.0519(7)	0.0464(6)	0.0033(6)	0.0146(5)	0.0027(6)
Co(2)	2*d*	0	1/2	1/2	0.0446(6)	0.0370(6)	0.0349(5)	0.0007(5)	0.0105(4)	0.0055(5)
Mn	4*e*	–0.05309(6)	0.03382(7)	–0.25232(4)	0.0476(5)	0.0483(6)	0.0562(5)	–0.0037(4)	0.0140(4)	0.0003(4)
Cl(1)	4*e*	–0.0936(1)	0.0802(1)	–0.37063(7)	0.061(1)	0.068(1)	0.0523(9)	–0.0110(8)	0.0050(7)	–0.0004(8)
O(1)	4*e*	0.1325(3)	0.0367(4)	–0.3424(2)	0.110(4)	0.151(5)	0.104(4)	–0.026(4)	0.071(3)	–0.022(4)
O(71)	4*e*	0.0255(3)	0.1586(3)	–0.2189(2)	0.062(3)	0.077(3)	0.068(3)	–0.022(3)	0.014(2)	–0.021(2)
O(72)	4*e*	0.1249(3)	0.2132(4)	–0.2649(2)	0.091(4)	0.095(4)	0.044(3)	–0.028(3)	0.016(2)	0.009(2)
O(81)	4*e*	0.0429(3)	–0.0825(3)	–0.2491(2)	0.061(3)	0.054(3)	0.090(3)	–0.008(2)	0.022(2)	–0.003(2)
O(82)	4*e*	–0.0920(3)	–0.1378(3)	–0.2693(2)	0.055(3)	0.058(3)	0.087(3)	0.004(2)	0.018(2)	0.006(2)
O(91)	4*e*	–0.0613(3)	0.0112(4)	–0.1455(2)	0.092(4)	0.076(4)	0.097(4)	0.017(3)	0.052(3)	0.016(3)
O(92)	4*e*	–0.1680(3)	0.0883(3)	–0.2203(2)	0.073(3)	0.073(3)	0.086(3)	–0.011(3)	0.026(3)	–0.015(3)
N(11)	4*e*	0.1147(3)	0.5302(4)	–0.0247(2)	0.043(3)	0.068(3)	0.042(2)	0.007(2)	0.014(2)	0.006(2)
N(12)	4*e*	0.1922(3)	0.5139(3)	0.0227(2)	0.039(2)	0.047(3)	0.043(2)	0.003(2)	0.017(2)	0.005(2)
N(21)	4*e*	0.0686(3)	0.3714(4)	0.0505(2)	0.045(3)	0.047(3)	0.059(3)	–0.001(2)	0.017(2)	0.002(2)
N(22)	4*e*	0.1522(3)	0.3851(3)	0.0887(2)	0.042(3)	0.040(3)	0.053(3)	0.009(2)	0.016(2)	0.008(2)
N(31)	4*e*	0.0642(3)	0.5764(3)	0.0912(2)	0.042(3)	0.055(3)	0.054(3)	0.015(2)	0.018(2)	–0.002(2)
N(32)	4*e*	0.1502(3)	0.5564(3)	0.1196(2)	0.037(3)	0.043(3)	0.044(3)	0.005(2)	0.011(2)	–0.003(2)
N(41)	4*e*	0.1126(3)	0.4722(3)	–0.4202(2)	0.045(3)	0.035(3)	0.044(2)	–0.003(2)	0.010(2)	0.011(2)
N(42)	4*e*	0.1168(3)	0.3842(3)	–0.3850(2)	0.039(3)	0.037(3)	0.040(2)	0.000(2)	0.007(2)	0.006(2)
N(51)	4*e*	–0.0677(3)	0.4448(3)	–0.4335(2)	0.052(3)	0.029(3)	0.047(3)	0.008(2)	0.017(2)	0.012(2)
N(52)	4*e*	–0.0328(3)	0.3637(3)	–0.3939(2)	0.050(3)	0.034(3)	0.037(2)	0.003(2)	0.017(2)	0.004(2)
N(61)	4*e*	0.0116(3)	0.3434(3)	–0.5204(2)	0.050(3)	0.040(3)	0.036(3)	0.002(2)	0.009(2)	0.004(2)
N(62)	4*e*	0.0297(3)	0.2763(3)	–0.4683(2)	0.053(3)	0.032(3)	0.040(3)	0.003(2)	0.012(2)	0.000(2)
C(1)	4*e*	0.1934(3)	0.4819(4)	0.0893(2)	0.042(3)	0.047(4)	0.040(3)	0.008(3)	0.015(2)	0.003(3)
C(2)	4*e*	0.0438(3)	0.3152(4)	–0.4009(3)	0.051(3)	0.033(3)	0.041(3)	0.000(3)	0.014(3)	0.005(2)
C(11)	4*e*	0.1362(4)	0.5604(4)	–0.0784(3)	0.058(4)	0.070(5)	0.043(3)	0.005(3)	0.021(3)	0.008(3)
C(12)	4*e*	0.2253(4)	0.5627(4)	–0.0669(3)	0.054(4)	0.068(5)	0.058(4)	0.004(3)	0.030(3)	0.014(3)
C(13)	4*e*	0.2593(3)	0.5332(4)	–0.0018(3)	0.040(3)	0.060(4)	0.055(3)	0.003(3)	0.024(3)	0.007(3)
C(21)	4*e*	0.0467(4)	0.2812(5)	0.0682(3)	0.056(4)	0.047(4)	0.080(5)	–0.003(3)	0.031(4)	0.003(4)
C(22)	4*e*	0.1138(4)	0.2377(5)	0.1174(3)	0.077(5)	0.047(4)	0.080(5)	0.004(4)	0.041(4)	0.015(4)
C(23)	4*e*	0.1799(4)	0.3058(5)	0.1298(3)	0.063(4)	0.053(4)	0.052(4)	0.017(3)	0.021(3)	0.014(3)
C(31)	4*e*	0.0445(4)	0.6451(4)	0.1313(3)	0.065(4)	0.047(4)	0.065(4)	0.013(3)	0.038(3)	0.006(3)
C(32)	4*e*	0.1171(4)	0.6683(5)	0.1853(3)	0.072(4)	0.052(4)	0.055(4)	–0.003(3)	0.028(3)	–0.007(3)

Table 3. Continued.

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(33)	4*e*	0.1827(4)	0.6102(4)	0.1760(3)	0.059(4)	0.047(4)	0.045(3)	–0.008(3)	0.017(3)	–0.002(3)
C(41)	4*e*	0.1909(4)	0.5132(4)	–0.3966(3)	0.048(3)	0.048(4)	0.051(3)	–0.003(3)	0.010(3)	0.001(3)
C(42)	4*e*	0.2455(4)	0.4540(5)	–0.3474(3)	0.042(3)	0.062(4)	0.058(4)	–0.009(3)	0.002(3)	0.009(3)
C(43)	4*e*	0.1965(3)	0.3718(5)	–0.3417(2)	0.039(3)	0.060(4)	0.038(3)	0.009(3)	0.004(3)	0.007(3)
C(51)	4*e*	–0.1384(4)	0.4671(4)	–0.4161(3)	0.053(4)	0.051(4)	0.048(3)	0.005(3)	0.018(3)	0.000(3)
C(52)	4*e*	–0.1502(4)	0.4027(4)	–0.3661(3)	0.054(4)	0.058(4)	0.054(4)	–0.005(3)	0.028(3)	0.009(3)
C(53)	4*e*	–0.0810(4)	0.3375(4)	–0.3530(3)	0.055(4)	0.052(4)	0.042(3)	–0.007(3)	0.022(3)	0.000(3)
C(61)	4*e*	0.0058(4)	0.2856(5)	–0.5737(3)	0.057(4)	0.057(4)	0.041(3)	–0.002(3)	0.014(3)	–0.012(3)
C(62)	4*e*	0.0211(4)	0.1843(5)	–0.5563(3)	0.071(4)	0.048(4)	0.059(4)	0.006(3)	0.022(3)	–0.019(3)
C(63)	4*e*	0.0360(4)	0.1809(4)	–0.4882(3)	0.064(4)	0.033(4)	0.056(4)	0.002(3)	0.013(3)	–0.008(3)
C(71)	4*e*	0.0981(4)	0.1960(4)	–0.2152(3)	0.052(4)	0.038(3)	0.050(4)	–0.003(3)	0.010(3)	–0.002(3)
C(72)	4*e*	0.1567(4)	0.2205(4)	–0.1472(3)	0.049(3)	0.037(3)	0.043(3)	0.002(3)	0.010(3)	–0.003(3)
C(73)	4*e*	0.1393(4)	0.1788(4)	–0.0911(3)	0.055(4)	0.052(4)	0.046(3)	0.008(3)	0.017(3)	0.001(3)
C(74)	4*e*	0.1949(5)	0.1991(5)	–0.0282(3)	0.086(5)	0.075(5)	0.046(4)	0.030(4)	0.018(4)	0.003(3)
C(75)	4*e*	0.2648(5)	0.2607(6)	–0.0212(4)	0.081(5)	0.076(5)	0.055(4)	0.023(4)	–0.007(4)	–0.028(4)
C(76)	4*e*	0.2816(4)	0.3026(5)	–0.0763(4)	0.055(4)	0.067(5)	0.087(5)	–0.008(4)	0.005(4)	–0.025(4)
C(77)	4*e*	0.2281(4)	0.2817(4)	–0.1395(3)	0.053(4)	0.049(4)	0.055(4)	–0.006(3)	0.008(3)	–0.009(3)
C(81)	4*e*	–0.0121(4)	–0.1541(5)	–0.2573(3)	0.051(4)	0.054(4)	0.048(4)	0.002(3)	0.011(3)	0.004(3)
C(82)	4*e*	0.0212(4)	–0.2608(5)	–0.2537(3)	0.054(4)	0.052(4)	0.036(3)	0.006(3)	0.007(3)	–0.005(3)
C(83)	4*e*	0.1062(4)	–0.2802(5)	–0.2521(3)	0.060(4)	0.073(5)	0.053(4)	0.007(4)	0.015(3)	–0.002(3)
C(84)	4*e*	0.1374(5)	–0.3772(7)	–0.2504(3)	0.080(5)	0.090(6)	0.058(4)	0.024(5)	0.009(4)	–0.014(4)
C(85)	4*e*	0.0818(7)	–0.4562(7)	–0.2514(3)	0.132(8)	0.075(6)	0.047(4)	0.040(6)	0.003(5)	–0.010(4)
C(86)	4*e*	–0.0022(6)	–0.4397(5)	–0.2525(3)	0.115(7)	0.046(5)	0.057(4)	–0.004(5)	0.001(4)	0.002(4)
C(87)	4*e*	–0.0342(4)	–0.3420(5)	–0.2546(3)	0.069(4)	0.055(4)	0.051(4)	–0.003(4)	0.012(3)	–0.003(3)
C(91)	4*e*	–0.1305(5)	0.0634(5)	–0.1614(4)	0.063(5)	0.058(5)	0.076(5)	–0.014(4)	0.034(4)	0.003(4)
C(92)	4*e*	–0.1654(4)	0.0997(5)	–0.1053(4)	0.068(5)	0.048(4)	0.088(5)	–0.013(4)	0.045(4)	–0.006(4)
C(93)	4*e*	–0.1258(5)	0.0694(6)	–0.0407(4)	0.078(5)	0.075(5)	0.101(6)	–0.016(4)	0.044(5)	–0.010(5)
C(94)	4*e*	–0.1525(7)	0.1083(7)	0.0117(4)	0.144(9)	0.097(7)	0.089(6)	–0.062(7)	0.063(6)	–0.032(6)
C(95)	4*e*	–0.2165(8)	0.1795(7)	–0.0005(6)	0.18(1)	0.077(7)	0.16(1)	–0.065(7)	0.13(1)	–0.059(7)
C(96)	4*e*	–0.2561(6)	0.2095(6)	–0.0639(6)	0.130(8)	0.061(6)	0.17(1)	–0.009(5)	0.112(8)	–0.019(7)
C(97)	4*e*	–0.2307(5)	0.1706(5)	–0.1166(4)	0.086(5)	0.052(5)	0.114(6)	–0.019(4)	0.058(5)	–0.011(4)

Acknowledgment. The Australian Research Council is thanked for support.

References

1. Moubaraki, B.; Murray, K. S.; Tiekink, E. R. T.: [bis-tris(pyrazolyl)methane-copper(II)] [chloro-bis(η^2-benzoato)-η^1-benzoato-manganate(II)] hydrate, $Cu(C_{10}H_{10}N_6)Mn(C_7H_5O_2)_3Cl \cdot H_2O$. Z. Kristallogr. NCS **218** (2003) 351-353.
2. Rardin, R. L.; Tolman, W. B.; Lippard, S. J.: Monodentate carboxylate complexes and the carboxylate shift: implications for polymetalloprotein structure and function. New J. Chem. **15** (1991) 417-430.
3. teXsan: Single Crystal Structure Analysis Software. Version 1.04. Molecular Structure Corporation. The Woodlands, TX, USA 1997.
4. Sheldrick, G. M.: SHELXS-86. Program for the solution of crystal structure. University of Göttingen, Germany 1986.
5. Sheldrick, G. M.: SHELXL-97. Program for crystal structure refinement. University of Göttingen, Germany 1997.
6. Walker, N.; Stuart, D.: An empirical method for corrrecting diffractometer data for absorption effects. Acta Crystallogr. A**39** (1983) 158-166.
7. Spek, T.: PLATON. A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands 2000.
8. Johnson, C. K.: ORTEPII. Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, 1976.