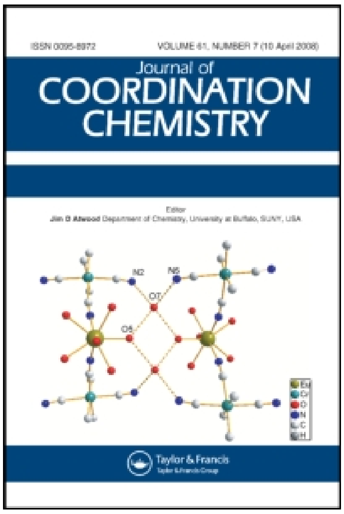

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Cungen Zhang[a]; Dan Wu[a]; Kaibei Yu[b]; Deyue Yan[a]
[a] Department of Chemistry, Shanghai Jiaotong University, Shanghai, P.R. China [b] Analysis Center, Chengdu Branch of Chinese Academy of Science, Chengdu, P.R. China

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SYNTHESIS, CRYSTAL STRUCTURE AND THERMOGRAVIMETRIC ANALYSIS OF MALEATO BRIDGED PHENANTHROLINE COMPLEXES

CUNGEN ZHANG[a,*], DAN WU[a], KAIBEI YU[b] and DEYUE YAN[a]

[a]*Department of Chemistry, Shanghai Jiaotong University, Shanghai 200240, P.R. China;* [b]*Analysis Center, Chengdu Branch of Chinese Academy of Science, Chengdu 610041, P.R. China*

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The polynuclear complexes poly-[(μ-maleato-$O:O'$)(1,10-phenanthroline-$N:N'$)-diaquacobalt] dihydrate, 1, and the isostructural manganese compound, 2, have been prepared and characterized by elemental analysis, IR spectra and thermogravimetric studies. The crystal structure of 1 is a one-dimensional infinite chain. Each Co atom is six-coordinated with two water molecules arranged *cis*. Co–O(water) distances are 2.0686(13) and 2.1531(13) Å and the Co–O(maleato) distances are 2.0954(13) and 2.1197(12) Å. The bite angle of phenanthroline to Co is 77.20(6)° with Co–N distances of 2.155(2) and 2.1531(14) Å. Complex 2 has an identical structure to complex 1. IR spectra indicate the presence of water molecules. Absorption peaks at 1546 and 1432 cm^{-1} for 1 and at 1540 and 1425 cm^{-1} for 2 are assigned to carbonyl asymmetric and symmetric vibrations, respectively. The two coordinated water molecules together with the two lattice water molecules for 1 are confirmed by thermogravimetric analysis.

Keywords: Cobalt(II); manganese(II); maleato; phenanthroline; X-ray structure

INTRODUCTION

Polynuclear metal complexes are of great interest not only in elucidating the magnetic coupling between metal ions[1] but also as model compounds of the active site of multi-metallo-enzymes.[2] Many works have been published on the synthesis and magnetism of polynuclear complexes containing carboxylato-bridged ligands.[3] Binuclear carboxylato complexes and

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[*] Corresponding author. E-mail: zcungen@kali.com.cn.

triangular trinuclear basic acetates are well-known examples.[4] Nevertheless, there are only a few reports of maleato-bridged complexes and no one-dimensional complex has been reported.[5] During the course of our attempts to synthesize binuclear complexes containing polycarboxylato bridging ligands, we obtained a series of novel maleato-bridged polynuclear complexes most of which have been investigated by single-crystal X-ray analysis.[6] As part of this research, we report here the synthesis, crystal structure and thermogravimetric analysis of maleato bridged complexes of cobalt(II), [Co(II)-(phen)(maleato)$(H_2O)_2$] · $2H_2O$ and the related manganese(II) complex.

EXPERIMENTAL

Physical Measurements

Elemental analyses for were carried out with a Perkin-Elmer Model 240. IR spectra were recorded on a Perkin Elmer 1000 spectrophotometer with KBr discs. Thermal studies were made on a Perkin Elmer 7 Series system under N_2 and a heating rate of 20°C min^{-1}.

Synthesis of [Co(II)(phen)(maleato)$(H_2O)_2$] · $2H_2O$

To an aqueous solution of cobalt nitrate tetrahydrate (10 mmol, 20 cm^3) was added an aqueous solution of sodium maleate (10 mmol, 20 cm^3) with stirring for 30 min. To the solution was added an ethanolic solution of phen (10 mmol, 15 cm^3) with stirring. Well formed crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent. Yield: 80%. Found: C, 45.25; H, 4.42; N, 6.30; Co, 13.90 (%). Calcd.: C, 45.19; H, 4.27; N, 6.59; Co, 13.86 (%). IR (cm^{-1}): 3306 (s) (νOH); 3058 (w) (δCH), 1643 (w), 1624 (w), 1546 (asym. νCO); 1513 (m), 1432 (s) (sym νCO); 1402 (s), 1348 (m), 1305 (s), 1230 (s), 1188 (w), 1144 (w), 1105 (w), 730 (s), 682 (m), 641 (m), 622 (m), 556 (m), 485 (m).

Synthesis of [Mn(II)(phen)(maleato)$(H_2O)_2$] · $2H_2O$

To a boiling aqueous solution containing 1.16 g (10 mmol) of maleic acid was added 1.12 g (10 mmol) of manganese carbonate monohydrate with stirring for 0.5 h. To this mixture was added an ethanolic solution containing 1.98 g (10 mmol) of phenanthroline monohydrate with stirring for *ca.* 1 h. Good quality crystals were obtained from the filtrate after several days.

Yield: 88%. Found: C, 45.55; H, 4.40; N, 6.50; Mn, 13.00 (%). Calcd.: C, 45.56; H, 4.27; N, 6.65; Mn, 13.04 (%). IR (cm^{-1}): 3300 (s) (νOH); 3040 (w) (δCH), 1620 (w), 1540 (asym. νCO); 1510 (m), 1425 (s) (sym. νCO); 1390 (s), 1340 (m), 1300 (s), 1185 (w), 1140 (w), 1100 (w), 910 (w), 860 (s), 840 (s), 805 (w), 780 (s), 715 (s), 710 (s), 540 (s), 420 (w).

X-ray Crystallography

A pale yellow crystal having dimensions of 0.40 × 0.40 × 0.24 mm was mounted on a glass fibre. Unit cell parameters and the orientation matrix were determined by least-squares refinement using the setting angles of 25 centred reflections ($12° < 2\theta < 22.5°$) measured on a Siemens P4 diffractometer with graphite-monochromated Mo$K\alpha$ radiation. Intensity data were collected at 291 K using a ω–2θ scan technique up to a maximum 2θ of 52°. Three standard reflections were monitored for crystal and instruments stabilities after every 97 data measurements. In all cases no significant variation was found. Some 3585 reflections were measured ($h \rightarrow 0$ to 9, $k \rightarrow -9$ to 9, $l \rightarrow -16$ to 16) which after data reduction ($R_{int} = 0.010$) gave 3334 independent reflections. The intensity data were corrected for Lorentz and polarization effects and empirical absorption. Details of crystal data, intensity collection and refinement are listed in Table I. The 3331 reflections with $I > 2\sigma(I)$ were used in the refinement of 317 parameters. The crystal structure was solved by direct methods and Fourier difference syntheses, and refined by full-matrix least-squares techniques using anisotropic temperature factors. All hydrogen atoms were located in a difference map. The final cycle of refinement converged at $R = 0.024$ and $R_w = 0.062$. All calculations were carried out using SHELXS-86,[7] SHELXL-93[8] and ORTEP[9] programs. Complete tables of atomic coordinates and thermal parameters, exclude structure factors are available from the authors upon request.

RESULTS AND DISCUSSION

Structure Description

The crystal structure for complex **2**, space group $P\bar{1}$, $a = 8.119(1)$, $b = 8.157(1)$, $c = 13.632(1)$ Å, $\alpha = 99.08(1)$, $\beta = 87.11(1)$, $\gamma = 101.94(1)°$ and $V = 872.1(3)$ Å^3 is similar to that of complex **1** as shown in Table I. Herein we present the structural study of complex **1**. An ORTEP view of the

TABLE I Crystal data and structure refinement details for 1

Compound	[Co(II)(maleato)(phen)$(H_2O)_2$] · $2H_2O$
Colour/shape	Yellow/prismatic
Empirical formula	$C_{16}H_{18}O_8N_2Co$
Formula weight	425.25
Temperature	291 K
Crystal system	Triclinic
Space group	$P\bar{1}$
No. of reflections used for unit cell determination (θ range)	28(3.26°–16.65°)
a (Å)	8.033(2)
b (Å)	8.1950(10)
c (Å)	13.420(2)
α (°)	80.950(10)
β (°)	87.400(10)
γ (°)	78.320(10)
Volume (Å^3)	854.3(3)
Z	2
$D_{calcd.}$ (g cm^{-3})	1.653
μ(MoKα) (cm^{-1})	10.55
F(000)	438
Diffractometer	Siemens P4
Radiation	MoKα ($\lambda = 0.71073$ Å) Graphite monochromated
Scan type	ω
$2\theta_{max}$	52°
No. of reflections measured	Total: 3585; unique: 3334 ($R_{int} = 0.0101$)
Correction	Semi-empirical from psi-scans
Structure solution	Direct methods (SHELX-86)
Refinement	Full-matrix least-squares (SHELXL-93)
Refinement method	Full-matrix least-squares on F^2
Treatment of H atoms	Diff. map and refined isotropically
No. observations [$I > 2\sigma(I)$]	3331
No variables	317
Goodness-of-fit on F^2	1.066
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0242$, $wR2 = 0.0621$
R indices (all data)	$R1 = 0.0286$, $wR2 = 0.0669$
Extinction coefficient	0.0112(13)
Largest diff. peak and hole	0.259 and −0.218 e$^-$/Å^3

complex with atom numbering scheme is shown in Figure 1. Atomic coordinates and selected bond distances and angles are shown in Tables II and III, respectively. Each metal atom is coordinated by two maleate dianions related by translation along the b-axis, two water molecules and a phen (phen = phenanthroline) forming six-coordinate geometry. The maleate dianion bridges two neighboring Co(II) atoms in the crystal forming an infinite one-dimensional chain along the b-axis. Two water molecules coordinate to the central metal atom in *cis*-fashion with bond distances of 2.0686(13) and 2.1531(13) Å, respectively. Two carboxylate O atoms of two symmetry-related maleate dianions also coordinate to the Co(II) atom in

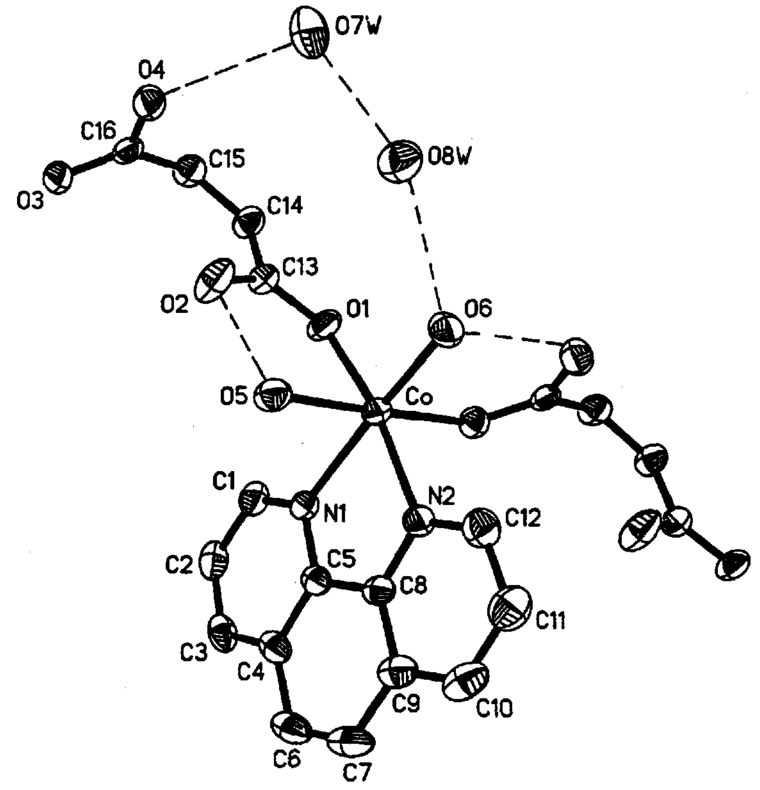

FIGURE 1 Molecular structure showing 50% probability displacement ellipsoids. H atoms on phen and maleate ligand are omitted for clarity.

cis-fashion with each carboxylate group acts as monodentate ligand in a *syn* manner. The Co–O(maleato) bond distances are 2.0954(13) and 2.1197(12) Å. The Co–N distances of 2.155(2) and 2.1531(14) Å are similar to those found in [Co(phen)$_3$](ClO$_4$)$_2$ · H$_2$O.[10] The bite angles of 77.02(5)° is also similar to that in [Co(phen)$_3$](ClO$_4$)$_2$ · H$_2$O (78.1°). Bond lengths and angles for phen moiety fall within the expected range. The distances between O5 and O2 of 2.584(3) Å, O6 and O4$^{\mathrm{i}}$ (symmetry code: (i) $x-1, y, z$) of 2.593(2) Å, O6 and O8 of 2.935(3) Å, O7 and O4 of 2.786(4) Å and O8 and O7 of 2.935(4) Å indicate hydrogen bonding interactions within the infinite chain as are shown in Figure 2. Neighboring chains are antiparallel to each other. Packing of the structure is mainly achieved by intra-chain hydrogen bonding interactions as shown in Figure 2.

TABLE II Atomic parameters and equivalent isotropic thermal parameters for 1

Atom	*x/a*	*y/b*	*z/c*	U_{eq} (Å^2)
Co	0.33454(3)	0.25738(3)	1.27372(2)	0.02480(9)
O1	0.12164(15)	0.4242(2)	1.31937(9)	0.0333(3)
O2	−0.0839(2)	0.2792(2)	1.31033(12)	0.0465(4)
O3	−0.50452(15)	0.41510(15)	1.30912(9)	0.0295(3)
O4	−0.3905(2)	0.2733(2)	1.45443(9)	0.0355(3)
O5	0.1781(2)	0.0825(2)	1.24578(10)	0.0327(3)
O6	0.3800(2)	0.1070(2)	1.41251(10)	0.0369(3)
O7W	−0.1958(2)	0.2420(2)	1.62629(13)	0.0506(4)
O8W	0.1336(2)	0.0531(3)	1.55500(12)	0.0495(4)
N1	0.3083(2)	0.3687(2)	1.11744(10)	0.0262(3)
N2	0.5458(2)	0.1109(2)	1.20174(10)	0.0273(3)
C1	0.1927(2)	0.4987(2)	1.07690(14)	0.0319(4)
C2	0.1850(2)	0.5577(2)	0.97305(15)	0.0366(4)
C3	0.3006(3)	0.4803(2)	0.90933(14)	0.0362(4)
C4	0.4269(2)	0.3417(2)	0.94956(13)	0.0309(4)
C5	0.4250(2)	0.2907(2)	1.05467(12)	0.0255(3)
C6	0.5549(3)	0.2539(3)	0.88899(14)	0.0380(4)
C7	0.6763(3)	0.1258(3)	0.93205(15)	0.0394(5)
C8	0.5533(2)	0.1543(2)	1.09982(12)	0.0250(3)
C9	0.6805(2)	0.0739(2)	1.03885(14)	0.0320(4)
C10	0.8070(3)	−0.0534(2)	1.0878(2)	0.0409(5)
C11	0.8013(3)	−0.0946(3)	1.1901(2)	0.0453(5)
C12	0.6667(3)	−0.0116(2)	1.24431(15)	0.0375(4)
C13	−0.0311(2)	0.4023(2)	1.33232(12)	0.0277(4)
C14	−0.1537(2)	0.5360(2)	1.37461(14)	0.0306(4)
C15	−0.3164(2)	0.5336(2)	1.39286(14)	0.0305(4)
C16	−0.4077(2)	0.3940(2)	1.38322(12)	0.0255(3)

TABLE III Selected bond distances (Å) and bond angles (°) for the complex

Bond lengths			
Co–O6	2.0686(13)	O2–C13	1.250(2)
Co–O1	2.0954(13)	O3–C16	1.259(2)
Co–O3^{i}	2.1197(12)	O4–C16	1.253(2)
Co–N1	2.1531(14)	C13–C14	1.483(2)
Co–N2	2.1554(15)	C14–C15	1.322(2)
Co–O5	2.1715(13)	C15–C16	1.502(2)
O1–C13	1.276(2)		
Bond angles			
O6–Co–O1	96.53(6)	O1–Co–O5	91.46(5)
O6–Co–O3^{i}	90.78(5)	O3^{i}–Co–O5	176.01(5)
O1–Co–O3^{i}	90.22(5)	N1–Co–O5	88.59(5)
O6–Co–N1	168.64(6)	N2–Co–O5	89.06(5)
O1–Co–N1	93.27(5)	C13–O1–Co	128.24(11)
O3^{i}–Co–N1	94.93(5)	C16^{i}–O3^{i}–Co	128.94(11)
O6–Co–N2	93.21(6)	C1–N1–Co	127.98(12)
O1–Co–N2	170.26(5)	C5–N1–Co	114.07(11)
O3^{i}–Co–N2	89.90(5)	C12–N2–C8	117.6(2)
N1–Co–N2	77.02(5)	C12–N2–Co	128.25(12)
O6–Co–O5	85.43(6)	C8–N2–Co	114.17(11)

Symmetry code: (i) $1 + x, y, z$.

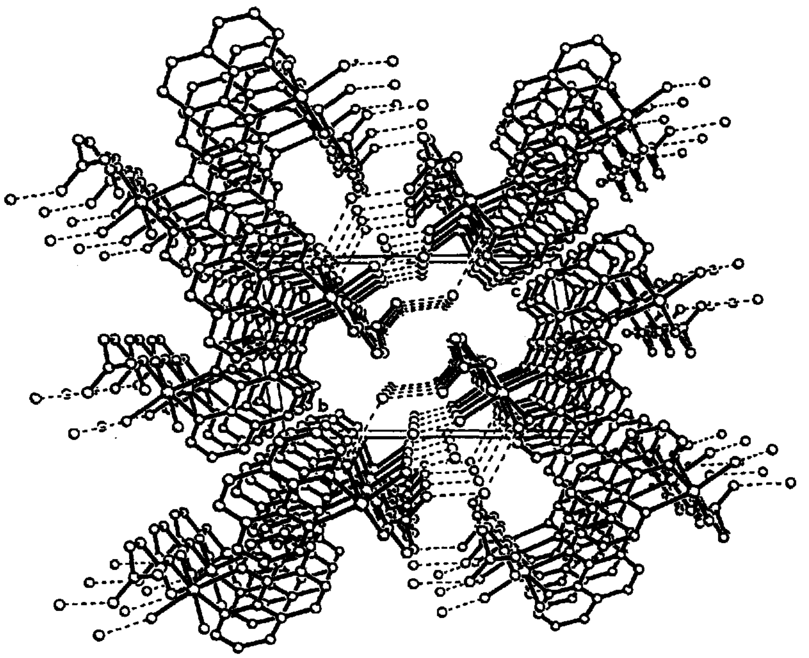

FIGURE 2 View of the title complex along the crystallographic *b*-axis illustrating the intramolecular hydrogen bonding framework.

Infrared Spectra and Thermogravimetric Analysis

IR spectra of the complex clearly show the existence of maleato dianion, 1,10-phenanthroline ligand and water molecules. The absorption bands at 1546 and 1432 cm^{-1} for complex **1** and those at 1540 and 1425 cm^{-1} for complex **2** are assigned to O–C–O asymmetric and stretching vibrations of maleato moiety, respectively. Carboxylate groups can coordinate to metal ions in a number of ways and IR spectroscopy is a useful tool in diagnosing the nature of carboxylate coordination. The separation between $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ when significantly less than for the free carboxylate anion value is considered indicative of a bidentate bridging or chelating carboxylate group, and a separation more than the free anionic value is indicative of a unidentate ligand.[11] Our results seems to contradict this rule since both terminal carboxylate groups are unidentate ligands at first glance. Careful examination of the hydrogen bonding interactions among the carboxylate groups and the coordinated and uncoordinated water molecules suggests that these interactions may be regarded as involving semi-coordination of the second oxygen atom of the carboxylate groups[11] and the IR spectra are in accordance with the above-mentioned view.

Thermogravimetric analysis for complex **1** indicates that the complex loses lattice water molecules at 60°C followed by the two coordinated water molecules with a weight loss of 17.1%. The resulting residue remains stable between 130°C and 260°C when the organic moieties began to decompose (to 420°C with a weight loss of 19.3% attributed to the decomposition of the maleato ligand ($CO_2 + C_3H_2$) and comparable to reported dicarboxylate phenanthroline copper(II) complexes[12]). Between 426°C and 576°C, a weight loss of 6% is observed and may be assigned to the decomposition of phen. No further decomposition is observed up to 800°C.

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