

# Metal $\alpha,\omega$ dicarboxylate complexes—3. Synthesis, characterization and single crystal X-ray investigation of [tetrakis(2-methylimidazolo) ( $\mu$ -diadipato)dicobalt(II)] monohydrate

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**Abstract**—Interaction of 2-methyl imidazole with tetraaquoadipatocobalt(II) polymer in water–ethanol mixture yielded dimeric cobalt(II) complex  $[\text{Co}(\text{COO}-(\text{CH}_2)_4-\text{COO}) (\text{C}_4\text{N}_2\text{H}_6)_2]_2 \cdot \text{H}_2\text{O}$ . The complex has been characterized by elemental analysis, IR spectroscopy and single crystal X-ray diffraction techniques. The crystal structure contains a dimer consisting of two  $\text{Co}(\text{cis-2Melm})$  units joined by two molecules of a folded dibasic acid forming an 18 membered ring. The metal center possesses a highly distorted octahedral geometry comprising two N-atoms from two 2-methylimidazoles and four O-atoms from two adipate anions forming strained four membered chelate rings. The molecule has a center of symmetry and forms a through channel with the maximum and minimum dimensions of 8.25(7) Å and 5.27(2) Å respectively. The hexagonally close packed dimeric units along a-axis includes a water molecule in the exterior channel. © 1997 Elsevier Science Ltd

**Keywords:** metal  $\alpha,\omega$  dicarboxylate complexes; crystal structure; N-donor ligands; dimer cobalt(II) complexes.

Extraordinarily versatile  $\alpha,\omega$  dicarboxylic acid ligands can adopt various modes of coordination such as chelating monodentate, bidentate forming polymeric species *via* bridging metal ions [1]. Designing of inorganic solids with novel polymeric network by linking metal ions with organic molecule is a potential field and has applications in catalysis, separation and electro-optical properties [2]. Appropriate multi-dimensional ligands with their moderate and strong coordination ability with metal centers and their versatile geometrical modes in bond formation can create various multi-dimensional polymers and supra-molecular architecture such as helices, grids, boxes, rods, tubes etc. [3]. Much work has been carried out in the coordination chemistry of monocarboxylic acids and a large number of monocarboxylate metal complexes have been structurally characterized [4], but the coordination chemistry of  $\alpha,\omega$  dicarboxylic acid and their structural characterization are relatively

few in literature. We are interested in the structural frame works of  $\text{Cu}^{\text{II}}$  and  $\text{Co}^{\text{II}}$  metal center ternary complexes, involving dicarboxylic acids of varying chain length and N-donor ligands such as bipyridyl, 2-methyl imidazole, imidazole, to understand the conformational flexibility of the dicarboxylic acids and various modes of network it can create by manipulating the N-donor ligands [5]. In this connection, the title compound was synthesized and structurally characterized.

## EXPERIMENTAL

All starting materials, cobaltous carbonate hydrate, adipic acid, and 2-methylimidazole, were commercially available and used without further purification. The solvent used was of AR grade.

### Synthesis

Tetraaquocobalt(II)adipate linear polymer [6] was synthesized by adding slowly hexanedioic acid

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[(COOH—(CH<sub>2</sub>)<sub>4</sub>—COOH), (adipic acid)] 2 mmol (0.292 g) in water-ethanol mixture to a heated suspension of cobaltous carbonate hydrate (CoCO<sub>3</sub>·H<sub>2</sub>O) 3 mmol (0.357 g) at 323 K. The mixture is refluxed at 343 K for 1 h. The light orange solution was filtered and the volume reduced to half resulted in light orange crystals. The purity of this compound was checked by elemental analysis. To 1 mmol (0.275g) of tetraaquadipatocobalt(II) polymer in distilled water, 4 mmol (0.328 g) of 2-methylimidazole in water-ethanol mixture was added with continuous stirring. The mixture was refluxed at 325K for 1 h and the pink solution obtained was reduced to half the original volume to get pink crystals suitable for diffraction studies. The solubility of the complex in water, ethanol and other common polar and non-polar solvents was very low. Analytical data for the complex: Found: C, 43.62; H, 5.74 and N, 14.50% and Calcd: C, 43.60; H, 5.71 and N, 14.53%.

#### Physical measurements

Elemental analysis of the complex was done using a C, H, N Carlo-Erba 1106 elemental analyzer and IR spectrum was recorded on Carl-Zeiss Specord M-80 spectrometer as KBr pellets (1%w/w).

#### X-ray crystallography

A pink plate of dimensions 0.32 × 0.20 × 0.14 mm was used for determination of space group and unit-cell dimensions as well as intensity data collections. Accurate cell dimensions were obtained by using 25 high angle reflections within the 2θ range 28–32°. Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite monochromatized Mo-K<sub>α</sub> radiation in the 2θ range 2–60°. After correcting for Lorentz and polarization effects, the intensities were corrected for absorption by an empirical absorption correction method [7] using three strong reflections near χ = 90°. The structure was solved by the heavy-atom method; the position of the metal ion was obtained using the Direct Methods program MULTAN-82 [8]. The structure was developed by alternating least-squares refinement and difference Fourier synthesis. Most of the hydrogen atoms were located in the difference Fourier map, after complete convergence of anisotropic refinement of the non-hydrogen atoms, a few were fixed stereochemically. Full matrix anisotropic refinement of non-hydrogen atoms, while keeping hydrogen atoms fixed using a unit weighting scheme, resulted in the convergence ((Δ/σ)<sub>max</sub> = 0.02). The crystallographic data for the complex are summarized in Table 1. All computations were carried out on a PDP/11-73 computer employing structure determination package available from Enraf-Nonius [9].

## RESULTS AND DISCUSSION

In the IR spectrum of the complex the most characteristic bands are from the antisymmetric and symmetric vibrations of the carboxylate group. The antisymmetric CO frequency is observed as a sharp peak at  $\nu_{\text{anti}}(\text{CO}) = 1560 \text{ cm}^{-1}$  and the symmetric CO frequency at  $\nu_{\text{sym}}(\text{CO}) = 1420 \text{ cm}^{-1}$ . The difference between the  $\nu_{\text{anti}}$  and  $\nu_{\text{sym}}$  ( $\Delta\nu = \nu_{\text{anti}} - \nu_{\text{sym}} = 140 \text{ cm}^{-1}$ ) indicates the chelating coordination mode of the carboxylate group [10].

An ORTEP [11] view of the molecule along with the numbering scheme is shown in Fig. 1 and Table 2 lists the bond lengths and angles in the molecule. The molecule is a centrosymmetric dimer; two Co *cis*-(2-Melm) units are bridged by two adipate dianions. Conformational angle (C(3)—C(4)—C(5)—C(6) = -61.9(5)°) clearly indicates the folding of the end carboxylate about C(4)—C(5) bond to achieve the metal coordination, in sharp contrast with the fully extended adipate monoanion forming doubly bridged polymer in *trans*-(Im)<sub>2</sub>Cu(adipate)<sub>2</sub> polymer [5]. It is observed that plane of the carboxylate end involving C(6) carbon almost perpendicular as observed from the dihedral angle (O(3)—C(6)—C(5)—C(4) = 90.4(5)°; O(4)—C(6)—C(5)—C(4) = -88.7(5)°). The geometry around the metal center can be described as highly distorted octahedral. The coordination octahedron is formed by two nitrogen atoms [N(1) and N(2)] of 2-methylimidazole units and four oxygen atoms from two carboxylates [O(1), O(2) and O(3), O(4)] forming four membered chelate rings. The distortion in the octahedral geometry is predominantly because of the smaller O—Co—O bite angles (O(1)—Co(1)—O(2) = 52.5(1)°, O(3)—Co(1)—O(4) = 59.0(1)°), taken by the end carboxylates forming four membered chelate rings. The large difference in bond lengths of the chelated oxygens with the metal center [Co(1)—O(1) = 2.401(4), Co(1)—O(2) = 2.056(3) Å and Co(1)—O(3) = 2.303(3), Co(1)—O(4) = 2.086(3) Å] may be attributed to the *cis* positions of O(1) and O(3). The bite distance of O(1)⋯O(2) and O(3)⋯O(4) are 2.165(3) and 2.170(1) Å, respectively, which agrees well with the other metal-carboxylate complexes and free carboxylic acids [12]. The steric effect of the projecting methyl group of the *cis* 2-methylimidazoles and the four membered chelate coordination of the carboxylate group is responsible for the significant deviation (11.4°) in the *cis* angle N(2)—Co(1)—N(1) = 101.4(1) from the ideal value.

The molecule has a center of symmetry at the point of intersection of Co(1)—Co(1') and C(3)—C(3') atoms. The two adipate dianions bridging the adjacent metal center makes an 18 membered ring with the maximum and minimum dimensions Co(1)—Co(1') = 8.23(7) and C(3)—C(3') = 5.25(7) Å, respectively. Packing of the molecules down crystallographic *a*-axis is shown in Fig. 2.

The dimeric units are hexagonally closely packed;

Table 1. Summary of crystallographic data

Molecular formula	C <sub>14</sub> H <sub>22</sub> N <sub>4</sub> O <sub>5</sub> Co
Molecular weight	385.29
Space group	Monoclinic, P2 <sub>1</sub> /c
Cell parameters	
<i>a</i> (Å)	9.856(2)
<i>b</i> (Å)	12.136(2)
<i>c</i> (Å)	14.817(2)
$\beta$ (°)	99.54(2)
<i>Z</i>	4
No. of reflection used and $2\theta$ range(°) used for unit cell parameters	25, 28–32
Radiation used, $\lambda$ (Å)	MoK $\alpha$ , 0.7107
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.486
Absorption Coeff, $\mu$ (cm <sup>-1</sup> )	10.10
Temperature (K)	295
Colour and description	pink plates
Crystal dimensions (mm)	0.32 × 0.20 × 0.14
Diffractometer	Enraf–Nonius CAD-4 diffractometer
Scan mode	$\omega/2\theta$
Absorption correction	empirical
Transmission min, max	99.95, 89.26
Measured reflections	1765
Observed reflections $I > 3\sigma(I)$	2034
$2\theta_{\max}$ (°)	60
<i>h</i> <sub>min</sub> , <i>h</i> <sub>max</sub>	0, 11
<i>k</i> <sub>min</sub> , <i>k</i> <sub>max</sub>	0, 13
<i>l</i> <sub>min</sub> , <i>l</i> <sub>max</sub>	–16, 16
No. of intensity control reflections, frequency and variation	3, 1h, nil
No. of orientation control reflections, frequency and variation	3, every 200 reflns., nil
Refinement on	<i>F</i>
Final <i>R</i>	0.037
Weighted <i>R</i>	0.041
Reflections used	1765
No. of parameters in least-squares	217
Hydrogen atom positions	not refined
( $\Delta/\sigma$ ) <sub>max</sub>	0.02
weighting scheme	unit weights
$\Delta\rho_{\max}$ (e/Å <sup>3</sup> )	0.448
$\Delta\rho_{\min}$ (e/Å <sup>3</sup> )	–0.274
Extinction correction	not applied
Source of atomic scattering factors	International Tables for X-ray crystallography Vol. IV, Kynoch Press, Birmingham (1974)

however, it leaves exteriorly through channels parallel to *a*-axis, because of the protruding methyl groups and water molecules are included in them. The water molecules form strong inter and intra molecular H-bonding networks with the carboxylate oxygens and the amino hydrogens(NH) of the 2-methylimidazole. The hydrogen bonding interactions with symmetry codes are shown in Table 3. Both 2-methyl imidazole units also exhibit stacking interactions; the partially overlapped moieties occur along the *a*-axis as well as along the *b*-axis.

### CONCLUSION

Mixed ligand binuclear complex of Co<sup>II</sup> with bridged dicarboxylate ions by the formation of four mem-

bered chelate ring with adjacent metal centers was synthesized and characterized by IR and single crystal X-ray diffraction techniques. The molecules are hexagonally close packed to form through channels parallel to the *a*-axis, which incorporates a water molecule by strong hydrogen bonding network. Further work on mixed ligand Co<sup>II</sup> complexes with N-donor ligands and  $\alpha,\omega$  dibasic acids with varying chain lengths is in progress. The flexible  $\alpha,\omega$  dicarboxylate can coordinate the metal center in a multitude of ways, an alteration in framework can be achieved by controlling the stereochemistry of the N-donor substituents on the metal ion. For example, a Co(Im)<sub>4</sub> unit forms a linear polymer linked by a singly bridged adipate anion [13], whereas a doubly bridged polymer is formed by linking Cu-trans(Im)<sub>2</sub> units by an

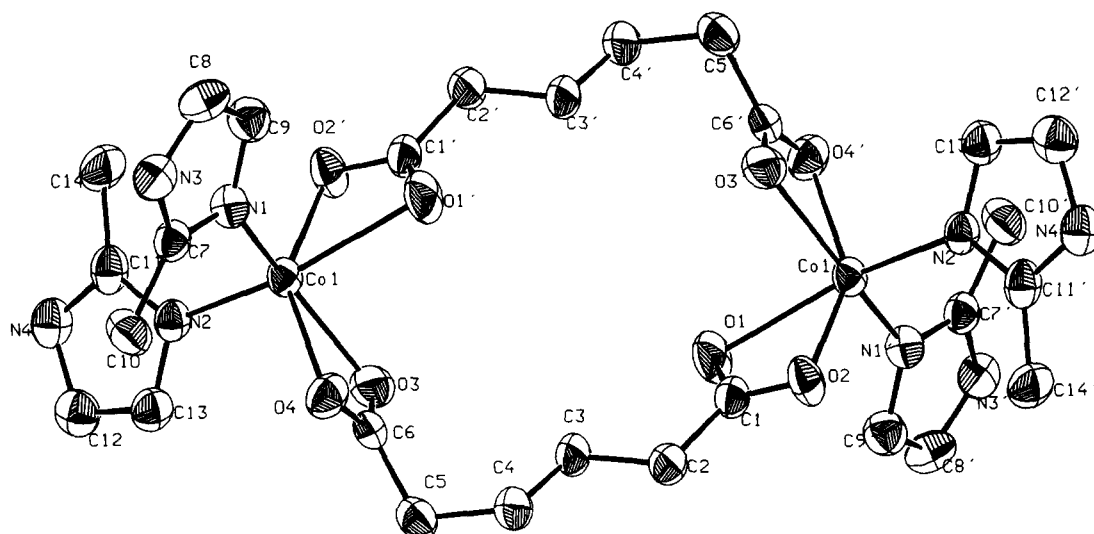


Fig. 1. ORTEP view of the molecule with 50% probability.

Table 2. Bond lengths (Å) and angles (°) for the complex with e.s.d.s in parentheses

Co(1)—O(2)	2.056(3)	Co(1)—N(2)	2.070(3)
Co(1)—O(4)	2.086(3)	Co(1)—O(1)	2.401(4)
Co(1)—N(1)	2.060(4)	Co(1)—O(3)	2.303(3)
O(1)—C(1)	1.233(5)	N(4)—C(12)	1.379(6)
O(2)—C(1)	1.274(5)	N(4)—C(11)	1.331(5)
O(3)—C(6)	1.248(5)	C(1)—C(2)	1.523(5)
O(4)—C(6)	1.275(5)	C(2)—C(3)	1.494(5)
N(1)—C(7)	1.319(5)	C(3)—C(4)	1.520(7)
N(1)—C(9)	1.369(6)	C(4)—C(5)	1.534(6)
N(2)—C(11)	1.331(4)	C(5)—C(6)	1.492(6)
N(2)—C(13)	1.376(6)	C(7)—C(10)	1.483(6)
N(3)—C(7)	1.352(6)	C(8)—C(9)	1.358(7)
N(3)—C(8)	1.363(9)	C(11)—C(14)	1.481(7)
N(4)—C(11)	1.331(5)	C(12)—C(13)	1.358(6)
O(1)—Co(1)—O(3)	86.4(1)	O(2)—Co(1)—N(2)	101.5(1)
O(1)—Co(1)—O(4)	94.2(1)	O(2)—Co(1)—C(6)	119.5(1)
O(1)—Co(1)—N(1)	88.5(1)	O(3)—Co(1)—N(1)	157.3(1)
O(1)—Co(1)—N(2)	158.6(1)	O(3)—Co(1)—N(2)	91.1(1)
O(2)—Co(1)—O(3)	93.4(1)	O(4)—Co(1)—N(1)	99.4(1)
O(2)—Co(1)—O(4)	143.2(1)	O(4)—Co(1)—N(2)	102.7(1)
O(2)—Co(1)—N(1)	102.4(1)	N(1)—Co(1)—N(2)	101.4(1)
O(3)—Co(1)—O(4)	59.0(1)	O(2)—Co(1)—O(1)	52.5(1)
C(7)—N(1)—C(9)	106.6(3)	O(3)—C(6)—C(5)	121.1(4)
C(11)—N(2)—C(13)	105.7(3)	O(4)—C(6)—C(5)	120.3(4)
C(7)—N(3)—C(8)	108.7(4)	N(1)—C(7)—N(3)	109.6(3)
C(11)—N(4)—C(12)	109.0(4)	N(1)—C(7)—C(10)	127.6(4)
O(1)—C(1)—O(2)	119.4(4)	N(3)—C(8)—C(9)	105.4(4)
O(1)—C(1)—C(2)	122.9(4)	N(1)—C(9)—C(8)	109.8(4)
O(2)—C(1)—C(2)	117.7(4)	N(2)—C(11)—N(4)	110.4(3)
C(1)—C(2)—C(3)	115.7(3)	N(2)—C(11)—C(14)	126.1(4)
C(2)—C(3)—C(4)	111.7(3)	N(4)—C(12)—C(13)	104.7(4)
C(3)—C(4)—C(5)	113.6(3)	N(2)—C(13)—C(12)	110.3(4)
C(4)—C(5)—C(6)	112.7(4)	N(4)—C(11)—C(14)	123.6(4)
O(3)—C(6)—O(4)	118.7(4)		

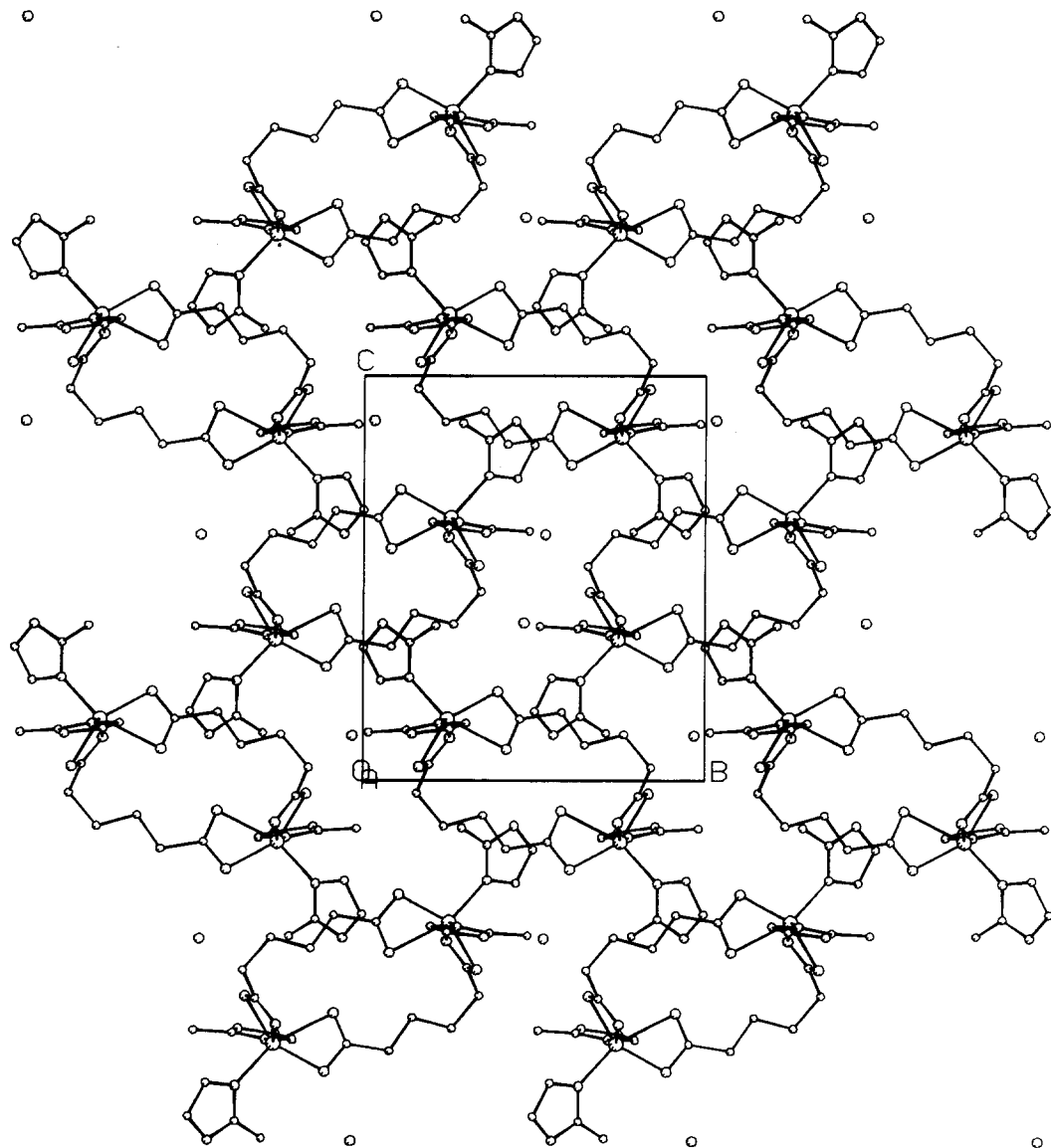


Fig. 2. Packing diagram viewed down along the  $a$ -axis.

Table 3. Hydrogen bonding data for the complex

H-Bonding	D—H (Å)	H...A (Å)	D...A (Å)	< D—H...A (°)	Symmetry code
N(3)—H(3)···O(5)	N(3)—H(3) = 0.935(4)	H(3)···O(5) = 1.835(4)	N(3)···O(5) = 2.763(6)	< N(3)—H(3)···O(5) = 164.0(3)	2-x, -y, 1-z
N(4)—H(4)···O(1)	N(4)—H(4) = 0.943(3)	H(4)···O(1) = 1.921(3)	N(4)···O(1) = 2.771(4)	< N(4)—H(4)···O(1) = 148.8(2)	x, y, z
O(5)—H(51')···O(2)	O(5)—H(51') = 0.874(3)	H(51')···O(2) = 1.959(3)	O(5)···O(2) = 2.792(5)	< O(5)—H(51')···O(2) = 158.8(3)	x, y, z
O(5)—H(52')···O(4)	O(5)—H(52') = 0.924(3)	H(52')···O(4) = 1.856(3)	O(5)···O(4) = 2.780(5)	< O(5)—H(52')···O(4) = 179.7(2)	1-x, 0.5+y, 0.5+1-z

extended adipate monoanion [5]. Dicarboxylate ligands thus continue to provide exciting polymeric species because of its extraordinarily versatile coordination properties.

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