Absorption correction:
empirical *via* ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.535$, $T_{max} = 0.723$
3797 measured reflections
3464 independent reflections

$\theta_{max} = 77.50°$
$h = 0 \rightarrow 7$
$k = -15 \rightarrow 14$
$l = -15 \rightarrow 15$
3 standard reflections
frequency: 120 min
intensity decay: 3.52%

Refinement

Refinement on F
$R = 0.0394$
$wR = 0.0473$
$S = 1.03$
3066 reflections
222 parameters
H atoms placed geometrically after each cycle
Chebychev polynomial (Carruthers & Watkin, 1979)

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}
Extinction correction: Larson (1970)
Extinction coefficient: 28 (2)
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 2. *Selected geometric parameters (Å, °) for (2)*

S1—N1	1.520 (1)	C1—C2	1.330 (2)
S1—O1	1.452 (1)	C2—C3	1.488 (2)
S1—C1	1.753 (2)	C2—C9	1.491 (2)
S1—C15	1.784 (2)		
N1—S1—O1	121.26 (8)	C1—S1—C15	105.86 (7)
N1—S1—C1	99.85 (8)	S1—C1—C2	125.9 (1)
O1—S1—C1	113.35 (8)	C1—C2—C3	119.8 (1)
N1—S1—C15	110.92 (8)	C1—C2—C9	123.9 (1)
O1—S1—C15	104.82 (8)	C3—C2—C9	116.3 (1)

The structure of (1) contains a disordered tetrahydrofuran molecule which is situated on a centre of symmetry. It was refined restraining the C—O and C—C bond lengths to their common mean. Displacement parameters were restrained to meet a null-motion criterion. Except for the H1 atom in compound (2), all H atoms (including solvent H atoms) are in calculated positions. The H1 atom in structure (2) was located in the difference map and refined isotropically restraining the C1—H1 bond length to 0.96 Å. The e.s.d.'s of the U_{eq} values were calculated using the method described by Schomaker & Marsh (1983).

For both compounds, data collection: *CAD*-4 *Express* (Enraf–Nonius, 1992); program(s) used to solve structures: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structures: *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985); molecular graphics: *SNOOPI* (Davies, Braid, Foxman & Powell, 1989).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: JZ1153). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Altomare, A., Cascarano, G., Giacovazzo, G., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435–436.

Boche, G. (1989). *Angew. Chem. Int. Ed. Engl.* **28**, 277–297.

Carruthers, J. R. & Watkin, D. J. (1979). *Acta Cryst.* A**35**, 698–699.

Chassaing, G. & Marquet, A. (1978). *Tetrahedron*, **34**, 1399–1404.

Davies, K., Braid, P., Foxman, B. & Powell, H. (1989). *SNOOPI. Molecular Plotting Program.* Oxford University, England.

Enraf–Nonius (1992). *CAD-4 Express. Diffractometer Control Software.* Enraf–Nonius, Delft, The Netherlands,

Gais, H.-J., Erdelmeier, I. & Lindner, H. J. (1986). *Angew. Chem. Int. Ed. Engl.* **25**, 935–938.

Gais, H.-J., Erdelmeier, I., Lindner, H. J. & Vollhardt, J. (1986). *Angew. Chem. Int. Ed. Engl.* **25**, 938–939.

Johnson, C. R. (1985). *Aldrichim. Acta*, **18**, 3–11.

Larson, A. C. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, S. R. Hall & C. P. Huber, pp. 291–294. Copenhagen: Munksgaard.

Müller, J. F. K., Batra, R., Spingler, B. & Zehnder, M. (1996). *Helv. Chim. Acta*, **79**, 820–826.

Müller, J. F. K., Neuburger, M. & Zehnder, M. (1995). *Helv. Chim. Acta*, **78**, 615–618.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Schomaker, V. & Marsh, R. M. (1983). *Acta Cryst.* A**39**, 819–820.

Watkin, D. J., Carruthers, J. R. & Betteridge, P. W. (1985). *CRYSTALS User Guide.* Chemical Crystallography Laboratory, University of Oxford, England.

Acta Cryst. (1997). C**53**, 422–425

Metal–α,ω-Dicarboxylate Complexes. II. *catena*-Poly[bis(imidazole-N^3)copper(II)-di-μ-adipato(1−)-O^1:O^6;O^6:O^1]

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Abstract

The structure of the title compound, $[Cu(C_6H_9O_4)_2(C_3H_4N_2)_2]_n$, is polymeric, joining two Cu^{II}–*trans*-(imidazole)$_2$ units by two extended adipate monoanions. The metal ion at the centre of symmetry has a highly distorted octahedral coordination; the two longer bonds are formed to the protonated carboxylate O atoms [Cu1—O3 2.499 (2) Å] and the octahedron is completed by bonds to two imidazole N atoms and two deprotonated carboxylate groups. The 'building block' of the polymer is an 18-membered ring of maximum dimensions 10.61 and 5.61 Å. Their molecular packing in space group *C*2/*c*, however, prevents channel formation of this size. The polymeric chains of the acid form very strong intramolecular hydrogen bonds *via* O3—H···O2 across the metal centre.

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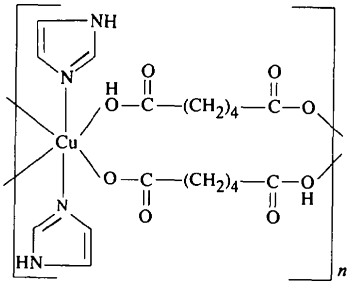
Comment

Designing new solids by linking metal ions with organic molecules is an emerging field with applications in catalysis, separation and electro-optical properties (Kim, Lee, Jung & Sohn, 1995). Appropriate multifunctional ligands with their strong coordination ability to metal centres can create supramolecular architectures such as helices, grids, boxes, tubes and interlocked systems (Fujita & Oruga, 1996). With this in mind, extraordinarily versatile α,ω-dicarboxylic acid ligands (Oldaham, 1987) as mono- or bidentate chelates forming polymeric species *via* bridging metal ions are under investigation in our laboratory (Suresh & Bhadbhade, 1997). The title compound, (I), was synthesized and structurally characterized with the aim of understanding the conformational flexibility of the dicarboxylic acid and the various modes of polymeric network it creates by manipulating various N-donor ligands on the metal.



(I)

An *ORTEPII* (Johnson, 1976) view of the building block of the polymer is shown in Fig. 1. The adjacent metal centres are bridged by two molecules of the adipate monoanion in their extended conformation, with the acid coordinating through only one of the O atoms at either end. The monoanionic nature of the dicarboxylic acid is well established by the presence of the H atom on O3 located in the difference Fourier map, and can be seen from a clear distinction between the protonated and deprotonated carboxylate geometries (Table 2), and the weaker coordination of O3(H) to the Cu^{II} ion [Cu—O3 2.499 (2) Å] compared with O1 [Cu—O1 1.992 (2) Å]. The coordination geometry of the Cu^{II} ion is highly distorted octahedral with the metal occupying the special position ($\frac{1}{4}$,$\frac{1}{4}$,0). The equatorial plane is formed by two centrosymmetrically related deprotonated and protonated O atoms of the carboxylates and two *trans*-axial imidazole N atoms [Cu—N 1.964 (2) Å] complete the hexacoordination.

Views of the molecular packing along different axes are shown in Figs. 2 and 3. The molecular packings of the β-forms of succinic acid, adipic acid, sebacic acid and glutaric acid may be recalled here. These form single polymeric chains connected *via* an O—H···O 'head-to-tail' type of hydrogen bonding between end carboxylates and have an interchain separation of approximately 5.5 Å (Morrison & Robertson, 1949*a*,*b*,*c*,*d*). A comparison of the present structure with that of adipic acid (Morrison & Robertson, 1949*b*) shows that the interchain spacing of 5.613 (8) Å is retained in both. The pattern of the linear polymer is altered, however, because of the Cu-*trans*-(Im)$_2$ spacers (where Im is imidazole). The staggered chains of adipic acids are more aligned by doubly bridging the successive metal centres. The positions of the N-donor substituents govern the mode of carboxylate linkages,

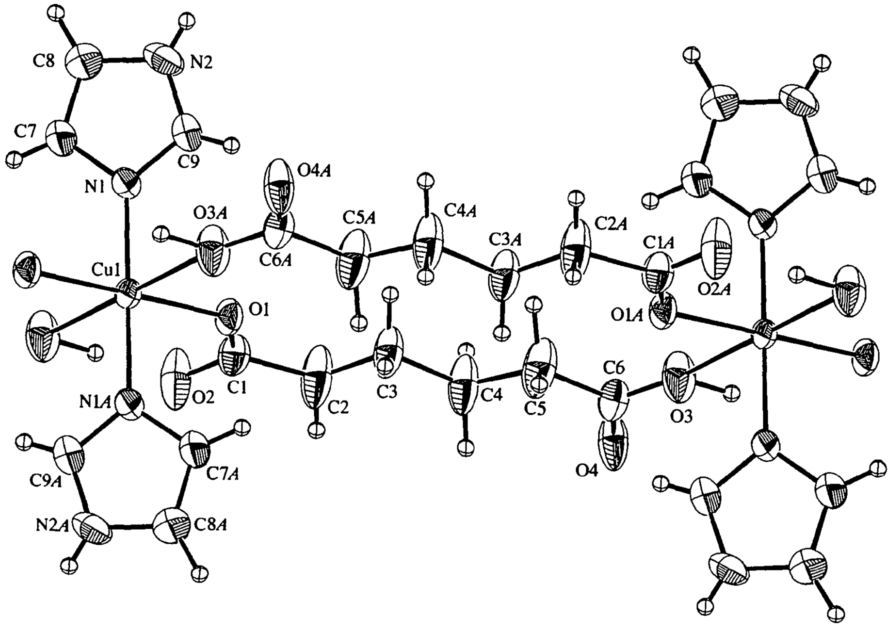


Fig. 1. The building block of the polymer (displacement ellipsoids are plotted at the 50% probability level).

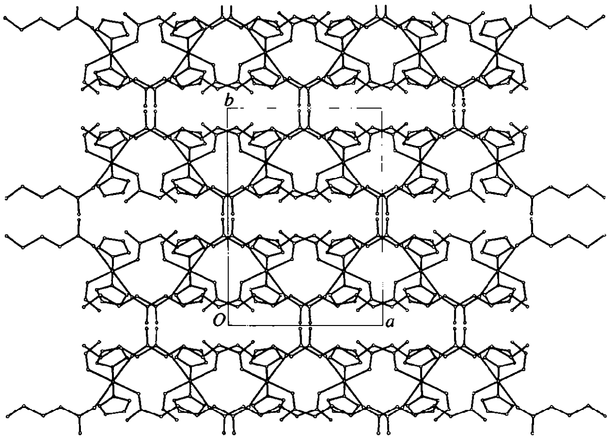


Fig. 2. Packing diagram viewed down the *c* axis.

for example, the same acid in its dianionic form is a doubly bridged dimer coordinated *via* both the O atoms of the carboxylates linking two Co–*cis*-(2-MeIm)$_2$ units (Suresh, Bhadbhade & Venkatasubramanian, 1997). The higher homologues of the acid can produce unique polymeric frameworks as reported in the structure of a 1,5-pentanedicarboxylic acid which links Cu(benzIm)$_2$ moieties by alternating single dianionic and double monoanionic bridges (Van Albada *et al.*, 1995).

As shown in Fig. 1, the monomeric unit consists of an 18-membered ring with maximum dimensions Cu···Cu 10.613 (2) Å and C4···C4 5.613 (8) Å. Overlapping of these units (Fig. 2) (displaced by half the unit cell), however, along the *a* axis reduces the effective dimensions of the channel and the possibilities for inclusions in them. The Cu–*trans*-(Im)$_2$ units are oriented in a zigzag manner along the *c* axis (Fig. 3) with the imidazole free H(N) atom hydrogen bonded to the coordinated oxygen [N2—H1N 0.73 (3), H1N···O4^{i} 2.08 (3), N2···O4^{i} 2.805 (4) Å and N2—H1N···O4^{i} 169 (4)°; symmetry code: (i) $\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$]. A striking feature in the polymer chain is the unusually strong intramolecular O3—H···O2 hydrogen bond [O3—H1O 1.01 (6), H1O···O2 1.46 (6), O3···O2 2.467 (3) Å and O3—H1O···O2 171 (5)°]. Such strong interactions are also observed in [Cu(DMG)$_2$(Im)] complexes (Morehouse, Polychronopoulou & Williams, 1980). A very weak coordination from this hydroxy group to Cu^{II} may be attributed to the strong intramolecular hydrogen bonding. Whether such polymeric chains would exhibit any special proton-transfer phenomenon reflected in the electrical conducting properties as observed in case of [Pt(dmg)$_2$(Im)$_2$] (Konno, Okamoto & Shirotani, 1989) under the variation of temperature or pressure is yet to be investigated.

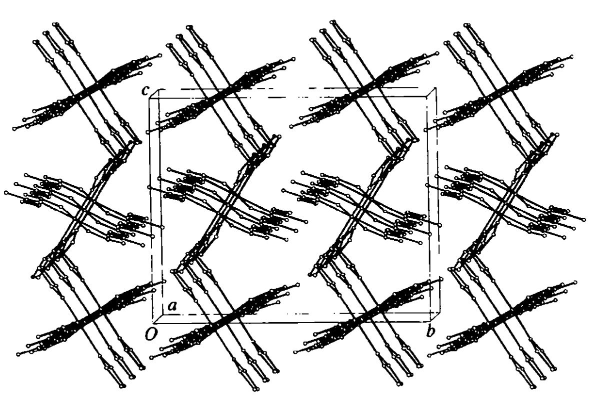


Fig. 3. Packing diagram viewed down the *a* axis.

Experimental

The title compound was synthesized by refluxing basic copper carbonate [$CuCO_3.Cu(OH)_2$], sodium hydroxide (NaOH), adipic acid ($C_6H_{10}O_4$) and imidazole ($C_3H_5N_2$) (molar ratio 1:2:2:2) in a water–ethanol mixture for 1 h. The violet–blue filtrate maintained at 295 K afforded crystals suitable for diffraction studies.

Crystal data

[$Cu(C_6H_9O_4)_2(C_3H_4N_2)_2$]
M_r = 489.97
Monoclinic
$C2/c$
a = 10.613 (2) Å
b = 15.402 (3) Å
c = 12.928 (4) Å
β = 93.35 (3)°
V = 2109.6 (9) Å^3
Z = 4
D_x = 1.543 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 11–13°
μ = 1.089 mm^{-1}
T = 293 (2) K
Plate
0.20 × 0.14 × 0.06 mm
Dark blue–violet

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
1375 measured reflections
1375 independent reflections
1205 reflections with $I > 2\sigma(I)$

$\theta_{\max}$ = 22.54°
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 13$
3 standard reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.0291
$wR(F^2)$ = 0.0768
S = 1.081
1375 reflections
194 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0404P)^2 + 3.2127P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.433 e Å^{-3}
$\Delta\rho_{\min}$ = −0.197 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
Cu1	1/4	1/4	0	0.0260 (2)
O1	0.4138 (2)	0.30353 (13)	0.0486 (2)	0.0335 (5)
O2	0.3401 (2)	0.4285 (2)	0.1066 (2)	0.0625 (8)
O3	0.1264 (2)	0.36690 (14)	0.0818 (2)	0.0537 (7)
O4	0.0326 (2)	0.48717 (15)	0.1279 (2)	0.0514 (6)
N1	0.2466 (2)	0.18386 (14)	0.1297 (2)	0.0291 (6)
N2	0.3028 (3)	0.0978 (2)	0.2575 (2)	0.0423 (7)
C1	0.4277 (3)	0.3779 (2)	0.0862 (2)	0.0386 (8)
C2	0.5604 (3)	0.4130 (3)	0.1057 (5)	0.0649 (12)
C3	0.6685 (3)	0.3591 (3)	0.0830 (4)	0.0506 (9)
C4	−0.2082 (3)	0.4088 (3)	0.1030 (4)	0.0603 (11)
C5	−0.0937 (3)	0.3636 (3)	0.0765 (4)	0.0629 (12)
C6	0.0273 (3)	0.4126 (2)	0.0979 (2)	0.0371 (8)
C7	0.1444 (3)	0.1652 (2)	0.1856 (3)	0.0441 (9)
C8	0.1790 (3)	0.1118 (2)	0.2641 (3)	0.0460 (9)
C9	0.3401 (3)	0.1411 (2)	0.1760 (3)	0.0398 (8)

Table 2. *Selected geometric parameters (Å, °)*

Cu1—N1	1.964 (2)	Cu1—O3$^{\rm i}$	2.499 (2)
Cu1—N1$^{\rm i}$	1.964 (2)	O3—C6	1.292 (4)
Cu1—O1$^{\rm i}$	1.992 (2)	O4—C6	1.212 (4)
Cu1—O1	1.992 (2)	O1—C1	1.249 (4)
Cu1—O3	2.499 (2)	O2—C1	1.253 (4)
N1—Cu1—N1$^{\rm i}$	180.0	N1—Cu1—O3	88.62 (9)
N1—Cu1—O1$^{\rm i}$	89.75 (9)	N1$^{\rm i}$—Cu1—O3	91.38 (9)
N1$^{\rm i}$—Cu1—O1$^{\rm i}$	90.25 (9)	O1$^{\rm i}$—Cu1—O3	87.81 (8)
N1—Cu1—O1	90.25 (9)	O1—Cu1—O3	92.19 (8)
N1$^{\rm i}$—Cu1—O1	89.75 (9)	O4—C6—O3	123.0 (3)
O1$^{\rm i}$—Cu1—O1	180.0	O1—C1—O2	125.4 (3)

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} - y, -z$.

All H atoms were located in the difference Fourier map and were refined isotropically.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *NRCVAX* (Gabe, Le Page, White & Lee, 1986). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

The authors wish to thank Professor P. Natarajan, Director of the Institute, for his encouragement.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: DE1043). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Fujita, M. & Oruga, K. (1996). *Bull. Chem. Soc. Jpn*, **69**, 1471–1482, and references therein.

Gabe, E. J., Le Page, Y., White, P. S. & Lee, F. L. (1986). *Acta Cryst*, **A43**, C-294.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kim, K. M., Lee, S. S., Jung, O. & Sohn, Y. S. (1996). *Inorg. Chem.* **35**, 11.

Konno, C., Okamoto, T. & Shirotani, I. (1989). *Acta Cryst.* **B45**, 142–147.

Morehouse, S. M., Polychronopoulou, A. & Williams, G. J. B. (1980). *Inorg. Chem.* **19**, 3558–3561.

Morrison, J. D. & Robertson, J. M. (1949*a*). *J. Chem. Soc.* pp. 980–986.

Morrison, J. D. & Robertson, J. M. (1949*b*). *J. Chem. Soc.* pp. 987–992.

Morrison, J. D. & Robertson, J. M. (1949*c*). *J. Chem. Soc.* pp. 993–999.

Morrison, J. D. & Robertson, J. M. (1949*d*). *J. Chem. Soc.* pp. 1000–1008.

Oldaham, C. (1987). *Comprehensive Coordination Chemistry*, Vol. 2, edited by G. Wilkinson, G. Gillard & J. A. McCleverty, p. 435. London: Pergamon Press.

Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures*. Pre-release version of 1992. University of Göttingen, Germany.

Suresh, E. & Bhadbhade, M. M. (1997). *Acta Cryst.* **C53**, 193–195.

Suresh. E., Bhadbhade, M. M. & Venkatasubramanian, K. (1997). In preparation.

Van Albada, G. A., Haasnoot, J. G., Reedjik, J., Biagini-Cingi, M., Manotti-Lanfredi, A. M. & Ugozzoli, F. (1995). *Polyhedron*, **14**, 2467–2473.

Acta Cryst. (1997). **C53**, 425–428

μ-1,4-Bis(diphenylphosphino)phenylene-*P*:*P*′-bis[*μ*$_3$-benzylidyne-octacarbonyl-*triangulo*-tricobalt(3 *Co*—*Co*)]

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Abstract

The title compound, *μ*-[1,4-phenylenebis(diphenylphosphino)]-*P*:*P*′-bis[*μ*$_3$-phenylmethylidyne-octacarbonyl-1κ^2*C*,2κ^3*C*,3κ^3*C*-*triangulo*-tricobalt(3 *Co*—*Co*)], $[\{Co_3(CO)_8(C_7H_5)\}_2(C_{30}H_{24}P_2)]$, lies about an inversion centre and consists of two approximately tetrahedral Co_3C units capped with phenyl groups and linked by a 1,4-bis(diphenylphosphino)phenylene ligand which replaces an equatorial carbonyl group on each cluster unit. The apical phenyl substituents and a phenyl ring from each P atom are arranged such that steric repulsion within the molecule is minimized.

Comment

As part of our investigation into the formation of conductive links between redox-active metal centres, we have targeted the substitution reactions of the readily reducible tricobalt–carbon cluster complexes