

Fred Garcia,^a Miguel A. Méndez-Rojas,^a Enrique González-Vergara,^b Sylvain Bernès^{b*} and Marco A. Quiroz^a

^aDepartamento de Química y Biología, Universidad de las Américas-Puebla, Ex-Hacienda Sta. Catarina Mártir, Cholula, 72820 Puebla, Pue., Mexico, and ^bCentro de Química, Instituto de Ciencias, Universidad Autónoma de Puebla, AP 1613, 72000 Puebla, Pue., Mexico

Correspondence e-mail:
sylvain@eros.pquim.unam.mx

Key indicators

Single-crystal X-ray study
T = 296 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
R factor = 0.030
wR factor = 0.076
Data-to-parameter ratio = 12.8

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

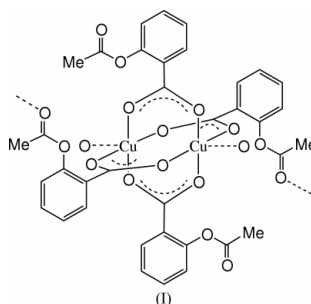
Di- μ -aspirinato-copper(II): a redetermination

The structure of the title compound, $[\text{Cu}(\text{C}_9\text{H}_7\text{O}_4)_2]_n$, has been redetermined at higher resolution and including the H atoms. The structure is identical, within the s.u. values, to that described 30 years ago, but is now reported more precisely.

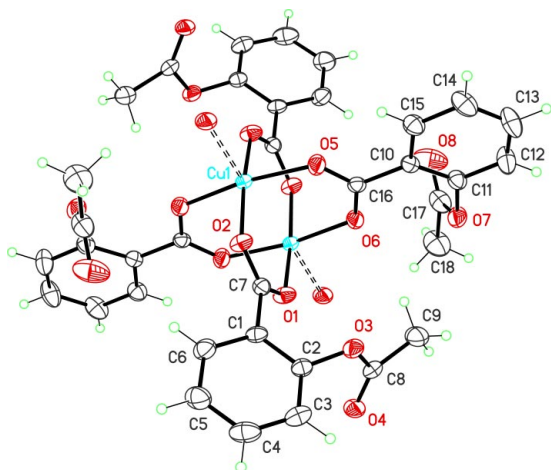
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Comment

The synthetic methodology of direct electrocatalysis is an electrochemical one-step process in which sacrificial anodes made of elemental metals are used to produce metallic ions in non-aqueous media by electrochemical oxidative dissolution. Although it is not a new technique, it is an interesting synthetic methodology, allowing the formation of coordination compounds in highly advantageous conditions. For instance, high purity and yields are achieved (Tuck, 1993; Garnovskii & Kharisov, 1999). In some cases, this route has been used successfully for the preparation of metal complexes that are difficult to obtain by conventional methods or that could not have been obtained otherwise (Fry, 1989; Méndez-Rojas *et al.*, 1999).

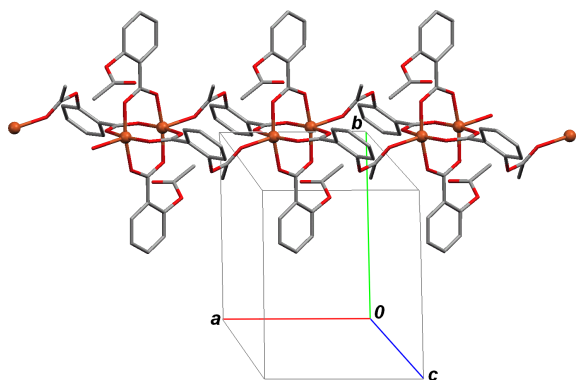


Such a case probably occurred when the title compound, (I), was first prepared and crystallographically characterized more than 30 years ago (Manojlović-Muir, 1967, 1973); the author notes that 'very small' crystals were obtained after the reaction of acetylsalicylic acid and copper salicylate tetrahydrate in aqueous ethanol. Diffraction data were collected using a sample with approximate dimensions $0.24 \times 0.07 \times 0.07 \text{ mm}$ to a resolution of *ca* 1 \AA . The structure was first refined isotropically (to $R = 0.10$), omitting the H atoms (Manojlović-Muir, 1967). A further report gives an anisotropic refinement (reaching $R = 0.078$), with standard deviations for the C—C bond lengths in the range $0.011\text{--}0.030 \text{ \AA}$ (Manojlović-Muir, 1973). We have now synthesized the same complex using the above-mentioned electrocatalysis route (see *Experimental*) and were able to obtain large single crystals suitable for X-ray characterization. Diffraction data were measured to 0.84 \AA resolution, yielding a refinement with s.u. values for C—C bond lengths in the range $0.003\text{--}0.005 \text{ \AA}$.


Figure 1

The molecular structure of (I), with displacement ellipsoids at the 40% probability level for non-H atoms, showing the labeling scheme for the asymmetric unit. One dimer is represented, including the complete coordination sphere for the metal centers. Dashed lines indicate the direction of polymerization.

The asymmetric unit of (I) contains one Cu atom and two aspirinate ligands, with the metal center close to an inversion center. Dimers with the formula $\text{Cu}_2(\text{C}_9\text{H}_7\text{O}_4)_4$ are then built through the inversion center (Fig. 1), in a way similar to that observed for the non-polymeric compound $[\text{Cu}_2(\text{aspirinate})_4(\text{DMF})_2]$, where DMF is *N,N'*-dimethylformamide (Viossat *et al.*, 2003). In (I), acetyl atom O4 bridges symmetry-related units, forming a one-dimensional polymeric structure with [100] as the base vector (Fig. 2). Neither significant interchain contacts nor hydrogen bonds are observed in the packing of (I); all $D-\text{H}\cdots A$ contacts display $\text{H}\cdots A$ separations greater than 2.40 Å. The closest stacking interaction is observed for C10–C15 benzene rings related by the symmetry operator $(1-x, -y, 1-z)$. The separation between the centroids of these rings [4.5921 (17) Å] is too long for this to be considered as a π - π interaction.


Figure 2

The crystal packing of (I). One polymeric chain is shown, with Cu atoms represented by spheres of arbitrary dimensions. H atoms have been omitted for clarity.

When comparing the geometry obtained for (I) on the basis of the 1973 refinement and that reported here, a remarkable similarity is obtained. A fit between asymmetric units (non-H atoms) gives an r.m.s. deviation of 0.035 Å, the largest deviation arising from atom C17 [0.077 Å]. Thus, within their respective precisions, the two refinements are identical. The considerably greater precision of the new refinement is largely due to the higher resolution of the diffraction data and the improved precision of the cell parameters. For instance, the $\text{Cu1}-\text{Cu1}^i$ separation within a dimer was reported as 2.617 (3) Å in 1973, whereas 2.6127 (6) Å was found in the present work [symmetry code: (i) $1-x, -y, -z$].

Experimental

Electrosynthesis experiments were performed in a conventional three-electrode cell with a Pt (99.999%, Aldrich) wire as auxiliary electrode (cathode), a saturated calomel electrode (SCE) as reference and a Cu (97%, Merck) foil as working electrode (sacrificial anode). The Cu foil was cleaned with dilute hydrochloric acid, washed thoroughly with threefold-distilled water and dried at 383 K before use. Acetonitrile (HPLC grade, Caledon), the reaction medium, was dried over molecular sieves and the supporting electrolyte was generated *in situ*. A small amount (*ca* 0.04 mmol) of the Na salt of the carboxylate ligand was generated by dissolving the respective acid (1.0 mmol) in dry acetonitrile (30 ml) and adding fresh metallic Na (*ca* 1.0 mg, 0.04 mmol, cleaned with dry ether). After 5 min of stirring at 298 K, the solid residues were separated by filtration. The resulting solution, containing the deprotonated ligand (*ca* 0.04 mmol) and the precursor acid (*ca* 0.96 mmol), was then used to fill the electrochemical cell. The electrolysis experiments were carried out at a constant current of 10 mA, which was imposed for a period of 180 min by using an EG&G PARC potentiostat-Galvanostat, model 362, affording (I) in 89–90% yield.

Crystal data

$[\text{Cu}(\text{C}_9\text{H}_7\text{O}_4)_2]$
 $M_r = 421.83$
 Monoclinic, $P2_1/c$
 $a = 8.2118$ (8) Å
 $b = 10.4158$ (10) Å
 $c = 21.484$ (2) Å
 $\beta = 104.341$ (8)°
 $V = 1780.3$ (3) Å³
 $Z = 4$

$D_x = 1.574$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 69 reflections
 $\theta = 4.4$ – 12.8 °
 $\mu = 1.27$ mm⁻¹
 $T = 296$ (1) K
 Prism, blue
 0.28 × 0.24 × 0.18 mm

Data collection

Bruker P4 diffractometer
 ω scans
 Absorption correction: ψ scan
 (XSCANS; Siemens, 1996)
 $T_{\min} = 0.711$, $T_{\max} = 0.795$
 5583 measured reflections
 3135 independent reflections
 2559 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$
 $\theta_{\text{max}} = 25.0$ °
 $h = -9 \rightarrow 4$
 $k = -12 \rightarrow 1$
 $l = -25 \rightarrow 25$
 3 standard reflections
 every 97 reflections
 intensity decay: 2%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.076$
 $S = 1.02$
 3135 reflections
 244 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0303P)^2 + 1.2189P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.29$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.34$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—O6 ⁱ	1.9581 (18)	O3—C8	1.359 (3)
Cu1—O1 ⁱ	1.9642 (17)	O3—C2	1.413 (3)
Cu1—O5	1.9646 (18)	O4—C8	1.198 (3)
Cu1—O2	1.9625 (17)	O5—C16	1.263 (3)
Cu1—O4 ⁱⁱ	2.2464 (18)	O6—C16	1.256 (3)
Cu1—Cu1 ⁱ	2.6127 (6)	O7—C17	1.371 (4)
O1—C7	1.263 (3)	O7—C11	1.399 (3)
O2—C7	1.255 (3)	O8—C17	1.191 (4)
O6 ⁱ —Cu1—O1 ⁱ	89.52 (8)	O1 ⁱ —Cu1—Cu1 ⁱ	84.02 (5)
O6 ⁱ —Cu1—O5	168.90 (7)	O5—Cu1—Cu1 ⁱ	82.32 (5)
O1 ⁱ —Cu1—O5	89.15 (8)	O2—Cu1—Cu1 ⁱ	85.22 (5)
O6 ⁱ —Cu1—O2	88.42 (8)	O4 ⁱⁱⁱ —Cu1—Cu1 ⁱ	176.07 (5)
O1 ⁱ —Cu1—O2	169.14 (7)	C7—O1—Cu1 ⁱ	122.83 (16)
O5—Cu1—O2	90.81 (8)	C7—O2—Cu1	121.74 (16)
O6 ⁱ —Cu1—O4 ⁱⁱ	97.20 (7)	C8—O3—C2	118.8 (2)
O1 ⁱ —Cu1—O4 ⁱⁱ	94.91 (7)	C8—O4—Cu1 ⁱⁱⁱ	130.28 (17)
O5—Cu1—O4 ⁱⁱ	93.89 (8)	C16—O5—Cu1	125.28 (17)
O2—Cu1—O4 ⁱⁱ	95.92 (7)	C16—O6—Cu1 ⁱ	120.80 (16)
O6 ⁱ —Cu1—Cu1 ⁱ	86.58 (5)	C17—O7—C11	116.9 (2)

Symmetry codes: (i) 1 - x, -y, -z; (ii) x - 1, y, z; (iii) 1 + x, y, z.

The refinement was carried out starting with the set of coordinates previously reported (Manojlović-Muir, 1973). H atoms were placed in idealized positions and treated as riding, with constrained distances and with $U_{\text{iso}}(\text{H})$ values fixed to $xU_{\text{eq}}(\text{parent})$ (C—H = 0.93 Å and

$x = 1.2$ for aromatic H atoms, and C—H = 0.96 Å and $x = 1.5$ for methyl H atoms).

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

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