Electronic Supplementary Material (ESI) for Dalton Transactions.

A Discrete Neutral Transition-Metal Citrate Cubane with an M_4O_4 Core; Coordinative Versatility of the $[M^{II}_4(\text{citrate})_4]^{8-}$ Fragment

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SUPPLEMENTARY INFORMATION

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EDUJUK: I.H.Hwang, P.-G.Kim, J.-C.Lee, C.Kim, Y.Kim, Acta Crystallogr.,Sect.E:Struct.Rep.Online (2012), 68, m1516.

CEFHUS: I.H.Hwang, P.-G.Kim, C.Kim, Y.Kim, Acta Crystallogr.,Sect.E:Struct.Rep.Online, (2012), 68, m1305.

LEHPAR: I.H.Hwang, P.-G.Kim, C.Kim, Y.Kim, Acta Crystallogr.,Sect.E:Struct.Rep.Online, (2012), 68, m1116.

I. Preparation, elemental analysis and IR data for compound 1:

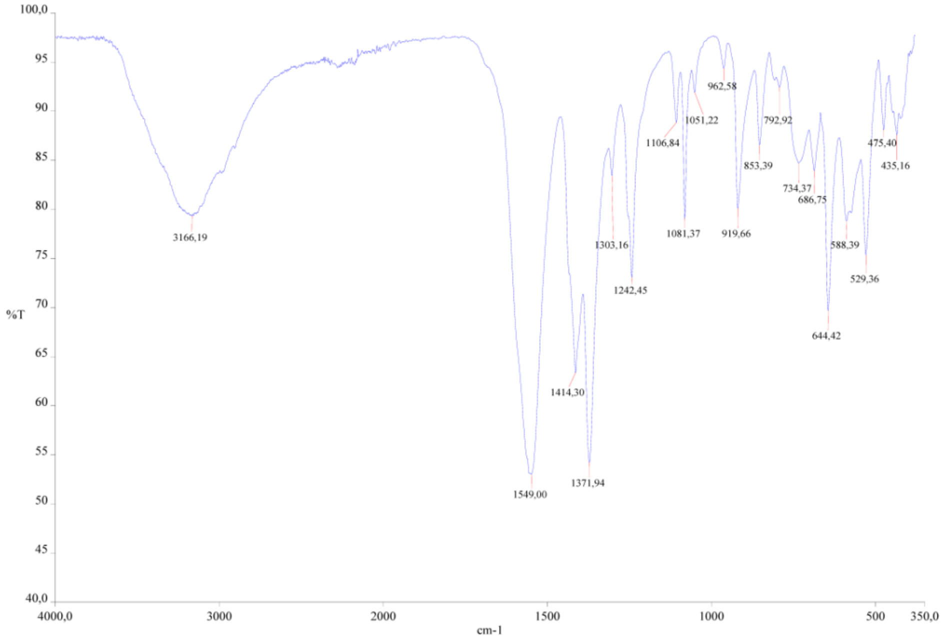
$[Mn^{II}_8(citrate)_4(H_2O)_{18}]\cdot$<u>$H_2O$, **1**</u>

All reactants were used as received from commercial sources without further purification.

The neutral cluster **1** was obtained as a white to light pink powder or as large, colourless single crystals depending on the procedure used. A quantity of 1.9 mol of $MnCO_3$ was added to a stirred solution of citric acid monohydrate (250 mL, 0.095 M). The mixture was heated to reflux under a stream of Ar for 5 h. and filtered. The solution was cooled under ambient conditions for several days, upon which it became orange and crystals of $(C_{12}H_{22}Mn_3O_{20})_n\cdot 4n(H_2O)$[1] were obtained. The suspension was filtered and the resulting supernatant was heated to reflux for 3 hours. At this point, a white precipitate appeared; reflux was detained while maintaining the heating, allowing evaporation of the solvent down to a volume of 50 mL. The suspension was filtered, giving a white to light pink powder of compound **1**. The supernatant, placed in a closed vial in an oven at 90°C, yielded large, colourless crystals of **1**.

Elemental analysis was performed on a Perkin Elmer 2400 CHNS/O analyser. Calculated analysis for $(C_{24}H_{54}Mn_8O_{47})$ is: C, 18.79%; H, 3.55%. Results obtained were C, 18.85%; H, 3.65%.

FT-IR spectra of compound **1** were measured on a Perkin-Elmer Spectrum 100 FT-IR Spectrophotometer with ATR accessory in the range of 4000-350 cm^{-1}.



IR spectrum of **1**

II. Structural characterization details

Thermogravimetric analyses (TGA) were carried out in a Universal V4.5A TA Instrument, model 2960 SDT V3.0F in the range of 25-500 °C

Powder x-ray data were collected on a RIGAKU D/max 2500 diffractometer equipped with a copper rotating anode, operating at 40 kV and 80 mA with a graphite monochromator. Measurements were made at 2θ values from 5 to 60° in steps of 0.03° with a rate of 1s/step.

Single crystal X-ray diffraction data were collected on an Xcalibur S3 CCD-based four-circle diffractometer (Oxford Diffraction and Agilent Technologies). The program CrysAlis Pro[2] controlled data collection and processing. The structure was solved *ab initio* by direct methods[3] and refined by full-matrix least-squares analysis.[4] Non-hydrogen atoms were refined with anisotropic displacement parameters. The methylene H atoms of the citrate ligands were placed at idealized positions and refined as riders with isotropic displacement parameters set to 1.2 times the equivalent isotropic U of their respective parent C atoms. The program Diamond[5] was used in the preparation of graphics.

In keeping with the rules laid out by the IUCr Commission on Crystallographic Data,[6] the two shortest axes perpendicular to the two-fold symmetry direction *b* were used as the *a*- and *c*-axes of the unit cell, which as a result is body centered with space group *I2.*

III. Re-refinement of the crystal structures of $M^{II}_2(H_2citrate)_2(H_2O)_4]\cdot N\text{-}N\cdot 2H_2O$ [M = Zn (CEFHUS),[7] Mn (EDUJUK),[8] N-N = 4-4′-ethene-1,2-diyldipyridine; M = Mn, N-N = 1,2-bis(pyridin-4-yl)ethane (LEHPAR)[9]

To date the vast majority of discrete molecular transition-metal (TM) citrate complexes have been found to be ionic, while neutral complexes have been found largely to be polymeric. We are aware of only three TM citrate complexes that have been reported as neutral, discrete molecules. These are $[M^{II}_2(H_2citrate)_2(H_2O)_4]\cdot N\text{-}N\cdot 2H_2O$ [M = Zn (CEFHUS in the Cambridge Database), Mn (EDUJUK), N-N = 4-4′-ethene-1,2-diyldipyridine; M = Mn, N-N = 1,2-bis(pyridin-4-yl)ethane (LEHPAR)]. As the reduced diffraction data are available at the journal web site, we have reconsidered the nature of these structures and have performed new refinements in light of discrepancies between our findings and the original reports.

We tested the possibility that in the following structures the hydrogen atom assigned to O5 of a citrate carboxyl group might in reality reside on pyridyl atom N11 of the base.

CEFHUS: We calculated an omit map, omitting H5, using all other parameters as found in the published refinement. This showed a double well between O5 and N11A.
We performed an ab initio re-determination of the positions and displacement parameters of H1O and H5 (which we ended up calling H5N, since it appeared near N11). First, H1O was located in a difference map and refined freely. Its displacement parameter, which was convergent, had a too-small value of about 0.006 A^2. A subsequent difference map revealed H1N near N11, as the first non-Zn-ghost peak in the difference map, Q7. This H atom refined to nearly ideal geometry and Uiso. The refinement was convergent. An omit map at this point showed slight density near the O5 position but nearly all of the positive density was at the new position of H1N, near N11.

EDUJUK: First, a difference map using the original model as published showed negative difference density over the region of the H atom in question, H5O, and pronounced positive difference density in the region that would be occupied by a putative H atom attached to N11. An omit map, omitting H5N from the original model, showed a double well pattern, but with the difference maximum in the region of O5 located very close to O5, about half-way along the O5---H5O bond.
We removed H1O (as a control atom) and H5O from the original model and refined the remainder. A difference map gave two peaks well differentiated from the others in density. The top peak had ideal geometry for the position of H1O, and the second peak had ideal geometry for a hydrogen atom attached to N11. These two atoms were incorporated into the model and refined freely -- both positions and Uiso. The refinement converged with good Uiso and nearly ideal geometries for the two H atoms, with the second now called H5N. An omit map following convergence, with H5N omitted, showed a clear one-well pattern for H attached to N11. A difference map, without omitting H5N, was nearly flat.

LEHPAR: For LEHPAR, we re-examined the data and the refinement using files downloaded from the Acta Cryst., Section E web site. Using the atoms from the original CIF, we observed what appeared to be a double well between O5 and N11c (1-x,1-y,2-z), with stronger difference density near N11c. Upon re-refining the structure, when H5 is freed from riding behavior it migrates toward N11c. When its Uiso is freed, H5 moves completely to a geometrically correct position bonded to N11c. Its Uiso refines convergently to a value of 0.068(8) Å ^2. At this point an omit map does not show significant density near O5. A difference map does not show significant negative difference density near the new position of H5. We conclude that the original double-well with a minor component near O5 was caused by leverage affecting other parameters when H5 was included in the incorrect position bonded to O5. A final test was to remove H1 and H5 completely from their reported positions and find them anew in a difference map following refinement of all of the other parameters, exactly as previously done by Kim et al. The two H atoms appeared as the top peaks in a difference map and were refined freely -- positions and Uiso. The resulting geometries and Uiso values were ideal.

We conclude that the H atom originally attributed to the carboxylate group O atom O5 is really located on the pyridyl nitrogen atom N11.

Refinement details are shown in Table S1.

Table S1. Comparison of the refinement details for compounds $M^{II}_2(H_2citrate)_2(H_2O)_4]\cdot N\text{-}N\cdot 2H_2O$ [M = Zn (**CEFHUS**), Mn (**EDUJUK**), N-N = 4-4´-ethene-1,2-diyldipyridine; M = Mn, N-N = 1,2-bis(pyridin-4-yl)ethane (**LEHPAR**).

	CEFHUS		**EDUJUK**		**LEHPAR**	
	[a]Original	**[b]New**	**Original**	**New**	**Original**	**New**
Restraints/parms	7 / 239	0/ 224	8 / 241	0 / 225	7 / 239	0 / 225
Goodness-of-fit	1.092	1.072	1.084	1.025	1.051	1.059
***R1, wR2* (obs)[c]**	0.0514, 0.1342	0.0506, 0.1319	0.0381, 0.0946	0.0364, 0.0896	0.0327, 0.0910	0.0307, 0.0846
***R1, wR2* (all)**	0.0604, 0.1395	0.0597, 0.1374	0.0482, 0.0975	0.0463, 0.0925	0.0351, 0.0924	0.0330, 0.0858
Δ/σ(max,mean)	0.000, <0.001	0.005, <0.001	0.001, <0.001	0.004, <0.001	0.001, <0.001	0.000, <0.001
$\Delta\rho$ range (e Å^{-3})	0.766, -1.356	0.770, -1.357	0.472, -0.632	0.279, -0.427	0.517, -0.417	0.361, -0.310

[a] Data for the refinement reported in the original publication, with one carboxylate protonated and the N atom from the N-N ligand unprotonated.

[b] Data for our re-refinement in which the H atom originally bonded to the carboxylate group of the citrate ligand has been located in the difference map and placed and refined freely coordinated to the N atom of the N-N ligand. That makes the three discrete compounds anionic instead of neutral as reported in the original publication.

[c] threshold I > 2σ(I).

IV. References

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Table S2. Crystallographic data for **1**.

Formula	$^{a}C_{24}H_{54}Mn_8O_{47}$	**Crystal size (mm^3)**	0.50 x 0.31 x 0.13
fw (g mol^{-1})	1534.19	**θ (min,max) (°)**	4.36, 28.85
Radiation	X-rays	**Reflns collected**	13682
Wavelength (Å)	0.71073	**Indep reflns**	5597
Crystal system	monoclinic	**R(int), R(σ)**	0.0144, 0.0218
Space group	*I2*	**Completeness (θ)**	0.985, 27.50
temp (K)	100(1)	**Abs corr**	multi-scan
***a* (Å)**	11.7817(2)	**T(min,max)**	0.4162, 0.7696
***b* (Å)**	9.9864(3)	**restraints/parms**	3, 419
***c* (Å)**	21.2165(3)	**Goodness-of-fit**	1.067
β (°)	101.519(2)	***R1, wR2* (obs)^b**	0.0154, 0.0402
V ($Å^3$), *Z*	2445.99(9), 2	***R1, wR2* (all)**	0.0155, 0.0402
ρ_{calc} (Mg/m^3)	2.083	**Δ/σ(max,mean)**	0.002, < 0.001
μ (mm^{-1})	2.126	**$\Delta\rho$ range (e $Å^{-3}$)**	0.407, -0.283
F (000)	1548.0	**^{c}Flack parameter**	0.017(4)

^{a} $[Mn^{II}_8(citrate)_4(H_2O)_{18}] \cdot H_2O$

^{b}threshold $I > 2\sigma(I)$.

^{c}Flack, 1983. Reference 10.

IV. Supplementary figures

Figure S1. Powder diffraction patterns for **1**, measured in 10-degree temperature steps from T = 20 ºC to T = 100 ºC, with a 30-minute stabilization period at each temperature before the diffraction measurements were made. Further measurements, made from T = 110 ºC to T = 180 ºC, were uninformative and are not shown.

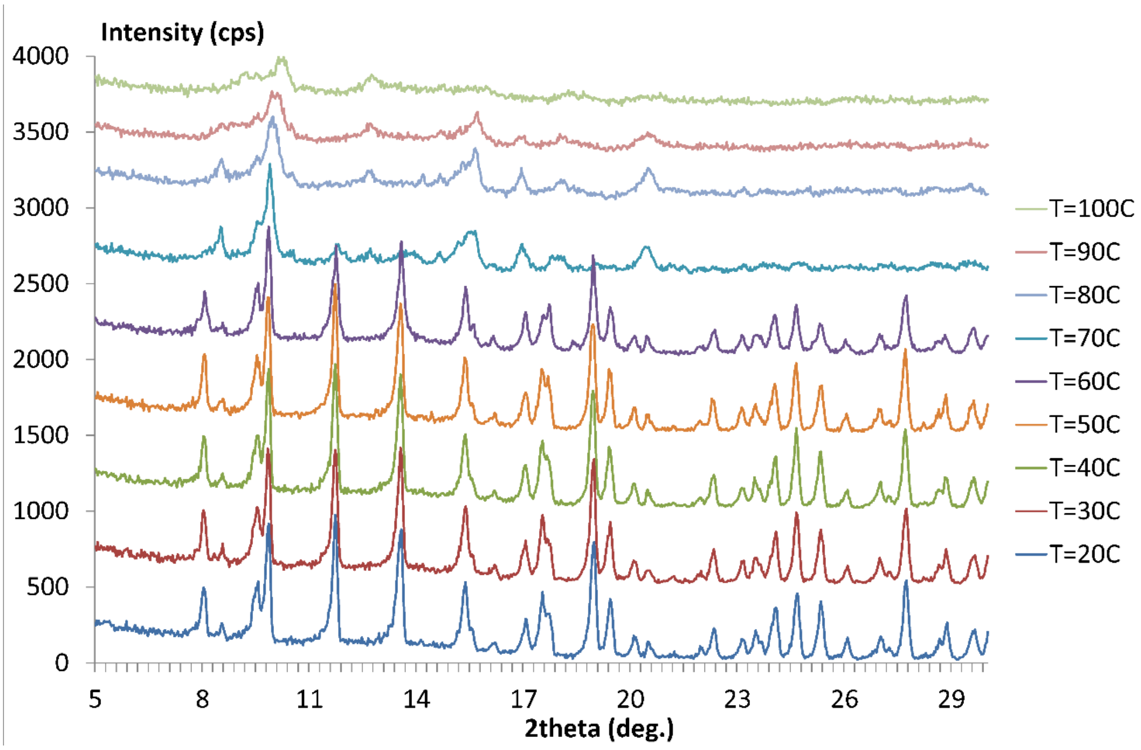

Figure S2. Powder diffraction patterns for **1**, measured in 2-degree temperature steps from T = 60 ºC to T = 76 ºC, with a 30-minute stabilization period at each temperature before the diffraction measurements were made.

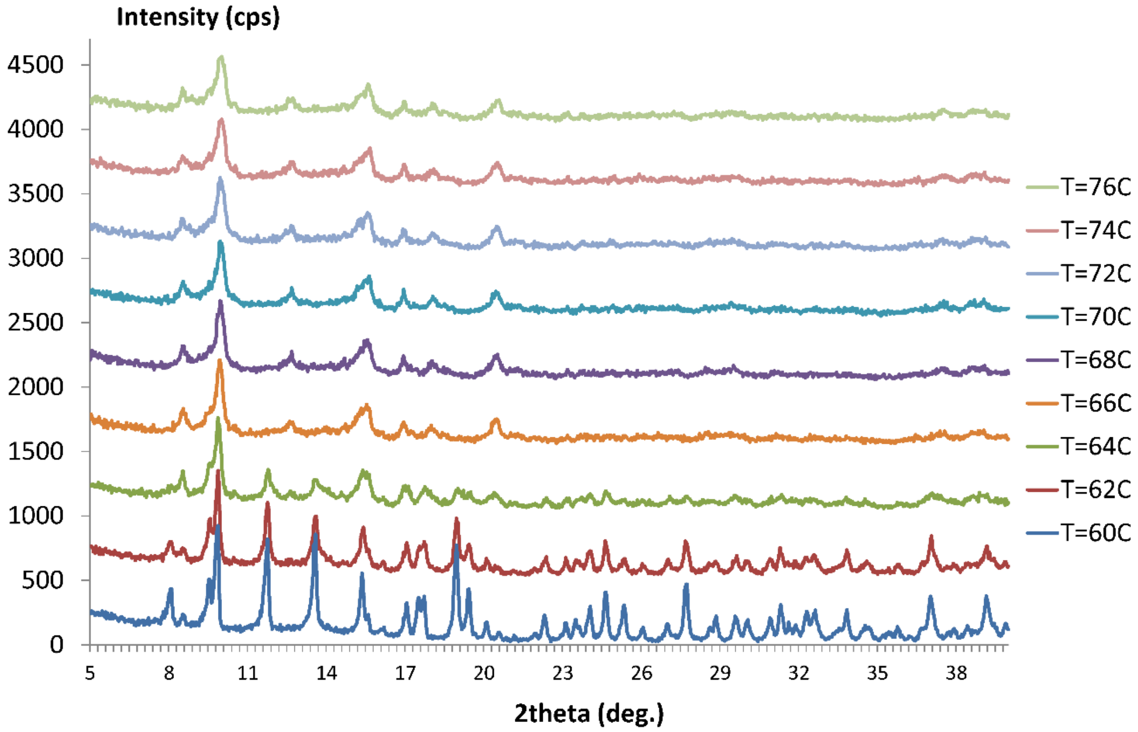

Figure S3. Powder diffraction patterns for **1**, before dehydration (T = 60 ºC), after dehydration (T = 68 ºC) and following rehydration in a humid atmosphere (T = 20 ºC).

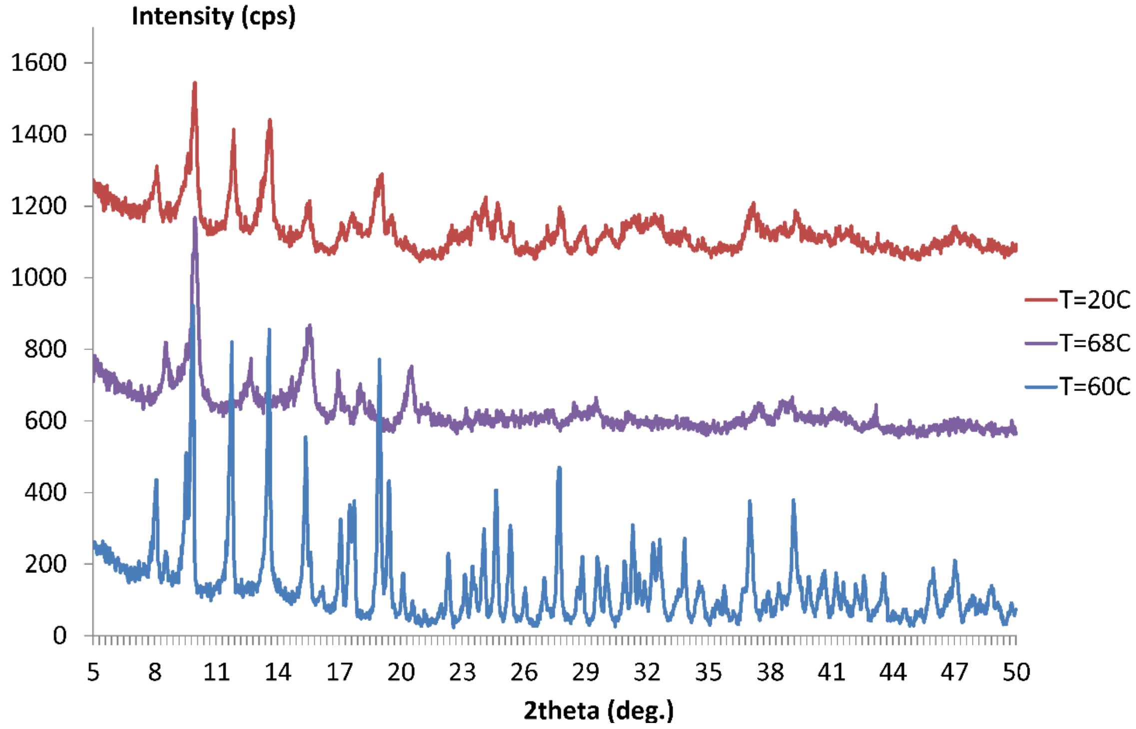

Figure S4. Thermogravimetric measurements for **1**.