

2D and 3D anilato-based heterometallic M(I)M(III) lattices: the missing link

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Supporting Information

X-ray powder diffraction. Compounds **1**, **3** and **4'**, (the major phase in the synthesis of **4**) were analyzed with the XRPD technique to check for phase purity in the samples used for the magnetic measurements and elemental analysis by comparing with the simulated diffractogram from the solved structures. The unit cell parameters obtained in the Pawley refinements are displayed in table S1. gives the following results: compound **1**: $a = 10.0477 \text{ \AA}$, $b = 23.7359 \text{ \AA}$, $c = 12.6179 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 104.55^\circ$, $\gamma = 90^\circ$, space group: $P2_1$, $R_{wp} = 2.556$, GOF = 1.781. Compound **3**: $a = 12.8607 \text{ \AA}$, $b = 25.8813 \text{ \AA}$, $c = 10.8061 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 93.01^\circ$, $\gamma = 90^\circ$, space group: $P2_1/c$, $R_{wp} = 1.616$, GOF = 1.278. Compound **4'**: $a = 9.7957 \text{ \AA}$, $b = 24.7850 \text{ \AA}$, $c = 12.5540 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 107.74^\circ$, $\gamma = 90^\circ$, space group: $P2_1$, $R_{wp} = 3.229$, GOF = 2.420.

Table S1. Unit cell parameters from Pawley refinements for compounds **1**, **3** and **4'** and those from single crystal diffraction data. The differences between the unit cells determined by single crystal data and powder diffraction data are caused by the different experimental temperatures (120 K vs. room temperature)

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	R_{wp}	GOF	sp. gr.
1 (single crystal)	9.8809	23.8659	12.4131	90	104.868	90			$P2_1$
1 (powder)	10.0477	23.7359	12.6179	90	104.55	90	2.556	1.781	$P2_1$
3 (single crystal)	12.7905	25.9152	10.6329	90	92.472	90			$P2_1/c$
3 (powder)	12.8607	25.8813	10.8061	90	93.01	90	1.616	1.278	$P2_1/c$
1 (single crystal)	9.8809	23.8659	12.4131	90	104.868	90			$P2_1$
4' (powder)	9.7957	24.7850	12.5540	90	107.74	90	3.229	2.420	$P2_1$

As clearly shown in figure S3, the diffractogram of compound **4'**, the major phase obtained in the synthesis of **4** can be indexed within the 2D structure found in compound **1**, indicating that both polymorphs: 2D (**4'**) and 3D (**4**), are obtained simultaneously.

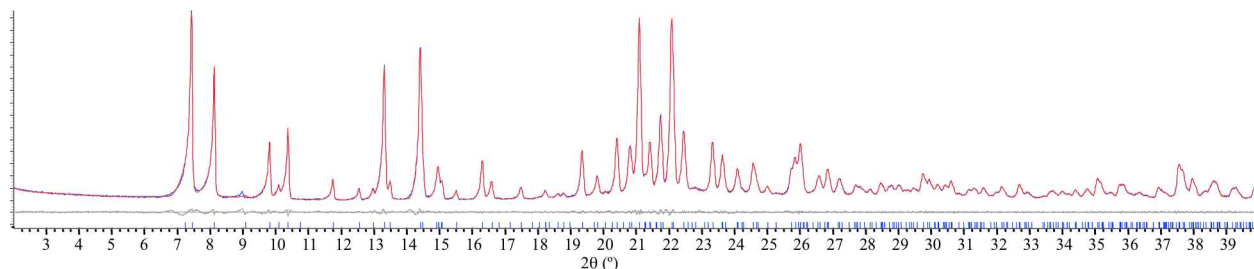


Figure S1. Observed (blue) and calculated (red) profiles and difference plots ($I_{obs} - I_{calcd}$; gray) of the Pawley refinements (2θ range $2.0-40.0^\circ$) for compound $(PBu_3Me)_2[NaCr(C_6O_4Br_2)_3]$ (**1**)

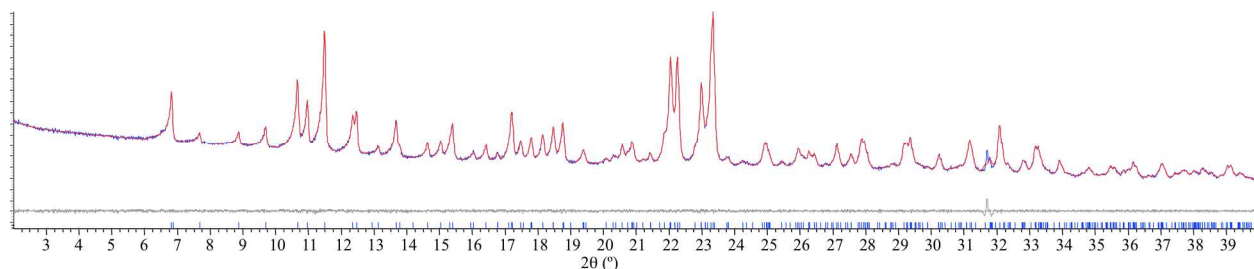


Figure S2. Observed (blue) and calculated (red) profiles and difference plots ($I_{obs} - I_{calcd}$; gray) of the Pawley refinements (2θ range $2.0-40.0^\circ$) for compound $(NEt_3Me)[Na(dmF)][NaFe(C_6O_4Cl_2)_3]$ (**3**)

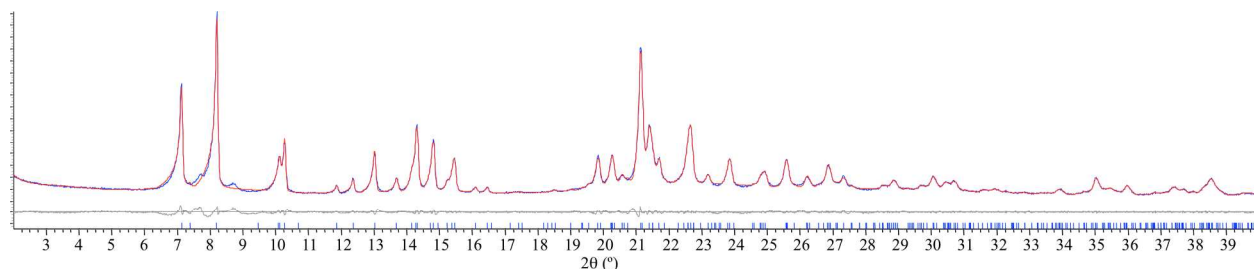


Figure S3. Observed (blue) and calculated (red) profiles and difference plots ($I_{obs} - I_{calcd}$; gray) of the Pawley refinements (2θ range $2.0-40.0^\circ$) for the 2D polymorph $(NBu_3Me)_2[NaCr(C_6O_4Br_2)_3]$ (**4'**).

IR spectra

In general, all the compounds show very similar IR spectra since the main bands arise from the anilato-based ligands.¹ They are also similar to those observed in the monomeric anions $[\text{M}^{\text{III}}(\text{C}_6\text{O}_4\text{X}_2)_3]^{3-}$ ($\text{M}^{\text{III}} = \text{Fe}$ and Cr ; $\text{X} = \text{Cl}$ and Br) since the coordination of these anions to Na^+ cations does not alter significantly the bonding in the $[\text{M}^{\text{III}}(\text{C}_6\text{O}_4\text{X}_2)_3]^{3-}$ anions.²⁻⁴

Compounds **1-3** and **4'**, besides the bands in the $2800\text{-}3000\text{ cm}^{-1}$ region, associated with the $\nu(\text{C-H})$ vibrations of the alkyl chains of the cations, show a weak to medium band in the region at ca. 1640 cm^{-1} corresponding to the $\nu(\text{C=O})$ vibration mode of the C=O groups weakly coordinated to the Na^+ ions.¹ Additionally, the four compounds show a very intense band at ca. 1520 cm^{-1} corresponding to the $\nu(\text{C=C})$ and $\nu(\text{C-O})$ vibrational modes as well as a strong band at ca. 1350 cm^{-1} attributed to the $\nu(\text{C-C})$ and $\nu(\text{C-O})$ modes. Finally, in the low energy region the four compounds show medium bands at ca. 1000 , 830 and 600 cm^{-1} corresponding to diverse C=O , C-O , C-C and C-X vibrational modes. As expected, in compound **3** these bands are slightly displaced to higher energies since the coordination modes of the chloroanilato ligands with the M^{I} cations are different to those observed in compounds **1**, **2** and **4'** are several anilato ligands.

The IR spectra of compounds **1-3** and **4'** are displayed in figures S1 and S2. Table S2 shows the main vibrational frequencies and their assignments.

Table S2. Selected vibrational frequencies (cm^{-1}) for compounds **1-3** and **4'**.

Ref.	M^{III}	X	$\nu(\text{C=O})$	$\nu(\text{C=C})$ $\nu(\text{C-O})$	$\nu(\text{C-C})$ $\nu(\text{C-O})$	$\nu(\text{C-C})$ $\nu(\text{C-O})$ $\delta(\text{C-X})$	$\delta(\text{C-O})$ $\delta(\text{C=O})$ $\nu(\text{C-X})$	$\rho(\text{C-X})$
1	Cr	Br	1644	1521	1346	985	809	603
2	Fe	Cl	1641	1525	1348	997	839	573
3	Fe	Cl	1633	1524	1361	1000	847	605
4'	Cr	Br	1642	1522	1348	986	810	604

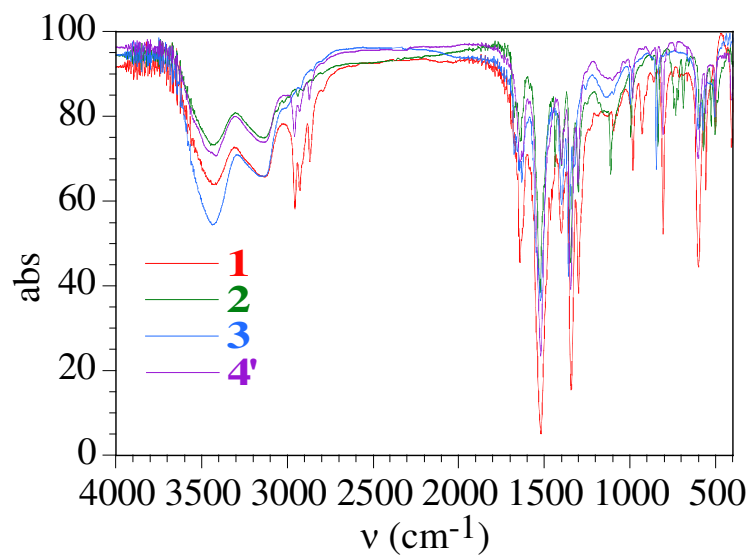


Figure S4. FT-IR Spectra in the 4000-400 cm^{-1} region for compounds **1-3** and **4'**

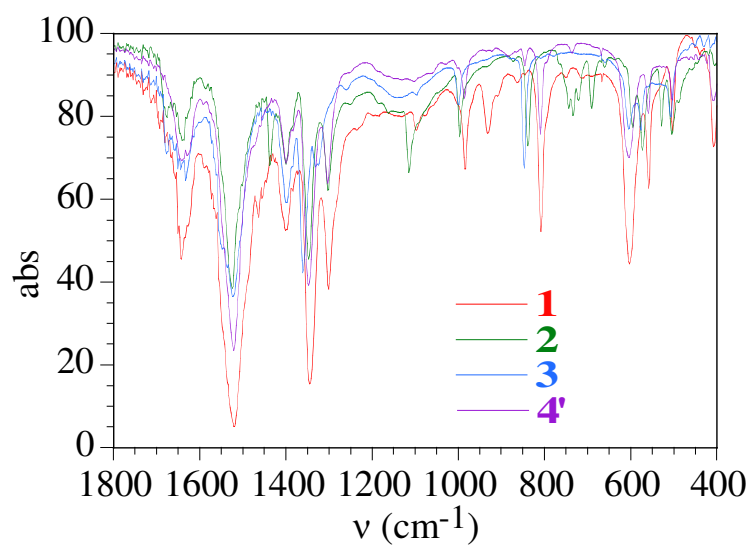


Figure S5. FT-IR Spectra in the 1800-400 cm^{-1} region for compounds **1-3** and **4'**

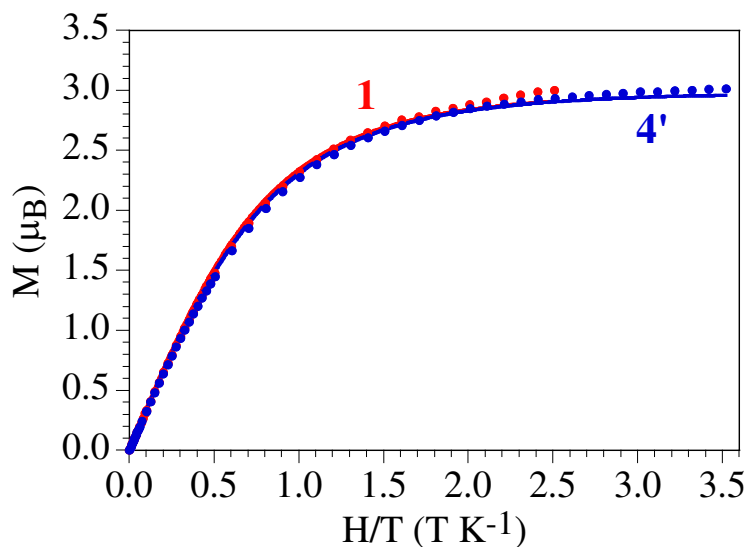


Figure S6. Isothermal magnetization of **1** and **4'** at 2 K. Solid lines are the best fit to the Brillouin function for $S = 3/2$ with $g = 1.984$ (for **1**) and 1.981 (for **4'**)

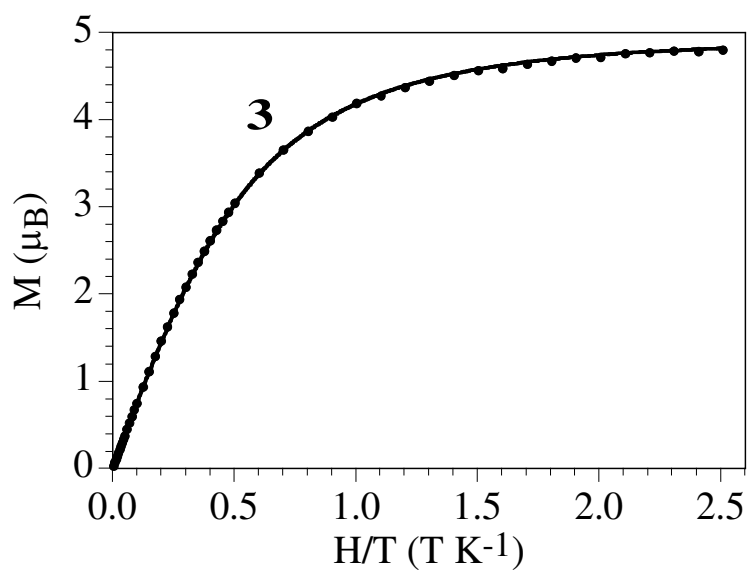


Figure S7. Isothermal magnetization of **3** at 2 K. Solid line is the best fit to the Brillouin function for $S = 5/2$ with $g = 1.957$

References

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