Supporting information – Pressure determination

The ruby fluorescence method was used to obtain the equation of state (EoS) of the title compound and this was then used as its own internal diffraction standard. From the P-V data obtained at the APS the equation of state of $[Co_3(dpa)_4Cl_2]$ ·dcm was determined between ambient pressure and 2.58 GPa using EosFit.¹ The fit parameters and results are listed in Table S1 and the results in Table S2.

P _{ruby} (GPa)	Crystal	V _{SCXRD} (Å ³)
0	А	2044.4
0.48	В	1926
0.82	А	1875
1.27	А	1834
2.02	А	1773
2.58	А	1733

Table S1. Experimental parameters.

Both the Birch-Murnaghan (BM) EoS, the natural strain (NS) EoS and the Vinet EoS were tested against the P-V data. For BM and NS fits various orders (first to fourth) of were used to fit the data, but only the models which describe the data best are listed in Table S2. The 3rd order Birch-Murnaghan (BM3) EoS and the 3rd order natural strain (NS3) EoS give essentially the same results and the NS3 model has been used to determine the pressures applied to crystals C and D.

Table S2. EosFit results from the three best models. V_0 is the unit cell volume at zero applied pressure, K_0 is the bulk modulus at zero applied pressure, K' is the first derivative of the bulk modulus and χ^2 is the agreement factor.

EoS model	V ₀ (Å ³)	K ₀ (GPa)	K'	χ² (%)	Corr. V ₀ -K ₀ / V ₀ /K'
					(%)
NS3	2044.30(678)	4.27(114)	27.80(987)	0.10	-57.11/44.4
BM3	2044.17(629)	5.09(98)	18.18(490)	0.16	-55.00/37.44
BM2	2032.7(146)	10.84(98)	4	3.3	-79.13/-
Vinet	2043.87(597)	5.83(71)	12.47(152)	0.23	-58.56/30.95

The pressure transmitting medium in these experiments was glycerol, which is only effectively hydrostatic up to 1.4 GPa, which means that three of the datasets describe non-hydrostatic conditions.² The bulk modulus was around 5 GPa in the three good models, which fits well with the general tendencies among molecular crystals.³

Supporting information - Theoretical calculations

Frontier orbital analysis

Unrestricted B3LYP⁴/6-311G** single point calculations were performed with Gaussian09⁵ using the molecular Co₃(dpa)₄Cl₂ geometries extracted from the experimental crystal structures obtained at the four different pressures (0.0 GPa, 0.32(3) GPa, 0.74(4) GPa and 3.2(1) GPa). The highest occupied molecular orbital (HOMO), the singly occupied molecular orbital (SOMO) and the lowest unoccupied molecular orbital (LUMO) are shown for the different wave functions in the pictures below (Iso-value MO 0.03. Element colors: green: Co, light blue: Cl, dark blue: N, grey: C. H atoms are omitted):





Figure S3 0.74 GPa geometry, B3LYP/6-311G** method





The HOMO, SOMO and LUMO turn out to be very similar in shape for the four geometries obtained at varying pressure, except for the 3.2 GPa geometry α -LUMO. Likewise, the energetic sequence of the frontier orbitals are very similar for the different geometries obtained at varying pressure; just above the α -HOMO follows the α -LUMO, and just above the β -HOMO follows the β -SOMO. The HOMO-LUMO and HOMO-SOMO energy gaps for the wave functions calculated for geometries obtained at the four different pressures are depicted in Figure S5. There are four gaps in total: α -HOMO- α -LUMO, α -HOMO- β -SOMO, β -HOMO- α -LUMO and β -HOMO- β -SOMO. The Co-Cl bond length at the same four pressures is shown in Figure S6.



Figure S5. Energy gaps with pressure.



Figure S6. The Co-Cl bond length.

The energy gaps in Figure S5 decreases as the pressure is increased, the only exception being the β -HOMO– α -LUMO energy gap (violet solid line in figure). This energy gap actually shows a local minimum at 0.32 GPa. But despite this local minimum, the β -HOMO– α -LUMO energy gap is the largest of the four energy gaps (α -HOMO- α -LUMO, α -HOMO- β -SOMO, β -HOMO- α -LUMO and β -HOMO- β -SOMO) even at 0.32 GPa. Therefore, it seems unlikely, that the β -HOMO– α -LUMO energy gap local minimum should be the explanation for the Co-Cl bond length increase at 0.32 GPa.

The four energy gaps (α -HOMO- α -LUMO, α -HOMO- β -SOMO, β -HOMO- α -LUMO and β -HOMO- β -SOMO) for the wave functions calculated at the four different geometries have values within 3.2 and 3.6 eV and do not seem to facilitate a thermal excitation at any of the different pressures investigated, since the thermal energy available is in the order of k_BT (0.03 eV at 298 K).

Excitation energies from Time-Dependent Hartree-Fock and Time-Dependent Density Functional Theory calculations

The LUMO energy and shape is generally ill-defined⁶ and precautions should be taken when interpreting HOMO-LUMO gaps obtained from ground state theoretical calculations like the B3LYP/6-311G** calculations in this study. Therefore, Time-Dependent Hartree-Fock (TD-HF)⁷⁻¹⁰ and Time-Dependent Density Functional Theory (TD-DFT)¹¹ calculations were also performed with GaussianO9 using the molecular Co₃(dpa)₄Cl₂ geometries extracted from the experimental crystal structures obtained at the four different pressures 0.0 GPa, 0.32 GPa, 0.74 GPa and 3.2 GPa to get better estimates of the excitation energies from the ground states to excited states. The basis sets and methods chosen were unrestricted TD-HF/6-311+G* and unrestricted TD-CAM-B3LYP¹²/6-311+G*. TD-HF might not be reliable for calculations on the molecule in question and correlated methods might give very different results. It is, however, not straightforward to perform correlated calculations (like Coupled Cluster) on excited states for the rather large Co₃(dpa)₄Cl₂ molecule in this study. Instead, TD-DFT with the long-range corrected hybrid functional CAM-B3LYP was chosen in addition to the TD-HF calculations. The smallest TD-HF and TD-DFT excitation energies obtained for each geometry is shown in Table 3.

Table 3. Vertical excitation energies (ΔE) and oscillator strength (F) to the lowest excited states from the ground state for the 0.0 GPa, 0.32 and GPa, 0.74 GPa and 3.2 GPa molecular Co₃(dpa)₄Cl₂ geometries. Excitation energies and oscillator strengths are calculated with the 6-311+G^{*} basis set and the TD-HF/TD-CAM-B3LYP methods. P is the pressure under which the crystal structure used to extract the molecular geometry for the calculation is determined.

	TD-HF/6-311+G*		TD-CAM-B3LYP/6-311+G*		
P (GPa)	ΔE (eV)	F	ΔE (eV)	F	
0.0	0.3188	0.0000	0.8552	0.0000	
	0.3244	0.0000	0.8706	0.0000	
	0.5003	0.0000	0.9049	0.0001	
0.32(3)	0.3273	0.0000	0.2371	0.0000	
	0.3377	0.0000	0.3536	0.0001	
	0.4914	0.0000	0.5542	0.0001	
0.74(4)	0.3092	0.0000	0.5779	0.0003	
	0.3263	0.0000	0.6087	0.0002	
	0.4950	0.0003	0.9576	0.0001	
0.32(3)	0.3584	0.0000	0.9967	0.0000	
	0.3825	0.0000	1.0219	0.0000	
	0.4189	0.0002	1.0598	0.0002	

The TD-HF excitation energies in Table 3 are within 0.3 - 0.5 eV for all four molecular geometries. However, TD-HF is known to overestimate excitation energies, often by ~ 1 eV.¹³ If this overestimation is taken in to account, it seems possible for thermal excitations to occur for the molecule in all four geometries in direct contrast to what the ground state B3LYP/6-311G** HOMO-LUMO and HOMO-SOMO gaps indicated. However, the TD-HF results do not suggest, that thermal excitations would be more likely for the 0.32 GPa geometry compared to the other geometries. Therefore, the TD-HF results do not provide an explanation for the unusual behavior of the Co-Cl bond length at 0.32 GPa. The TD-DFT excitation energies in Table 3.

NBO analysis

Natural bond orbital (NBO) analysis¹⁴⁻²⁰ of the B3LYP/6-311G^{**} 0.0 GPa / 0.32 GPa / 0.74 GPa / 3.2 GPa molecular geometry wave functions was performed by the program NBO 3.1²¹ implemented in Gaussian 09. The results are shown in Table S4 and Table S5. The NBO analysis provides the most probable Lewis structure and divides the NBOs into Lewis-type NBOs (core, lone-pairs and 2-center bonds) and non-Lewis NBOs describing the residual resonance delocalization effects. The donor-acceptor interactions in the NBO basis can be evaluated by performing second-order perturbation theory analysis. Donor orbitals are typically filled Lewis-type NBOs. Acceptor orbitals are typically empty non-Lewis NBOs. The second-order stabilization energy estimate, E(2), associated with the delocalization from the Lewis donor NBO to the non-Lewis acceptor NBO is a measure of the strength of the donor-acceptor interaction.^{14-20,22,23}

The NBO analysis encounters difficulties in identifying a satisfactory Lewis structure for all four wave functions. The natural Lewis structure accounts for only 96 - 97 % of the total electron density and the number of low-occupancy Lewis orbitals is relatively high. Low-occupancy refers to occupancy less than the occupancy threshold used in the Lewis structure search. It is typically 0.90 electrons for open-shell cases, but only 0.70 - 0.80 electrons in the present cases due to the poor Lewis structure description. For all four wave functions low-occupancy core orbitals (occupancy of less than 0.9990 electrons) are found on the three Co atoms in the chain. These results show the delocalized nature of the molecule and particularly the Co-Co-Co bond. There are no bonding NBOs between Cl and Co, but a number of donor – acceptor interactions are found. All four wave functions have three (two beta and one alpha) largely dominating o bonding donor – accepter interactions - each with a stabilization energy within 17.4 – 23.3 eV. This shows that the strongest delocalization (charge transfer) in the Co-Cl bond involves the interaction of Lewis lone pair electrons on Cl with empty non-Lewis lone pairs on Co. There are no clear difference between the donor-acceptor interactions for the wave function obtained from the 0.32 GPa geometry and the donor-acceptor interactions for the wave functions obtained from the 0.0 GPa and 0.74 GPa geometries. That is, there is no clear explanation for the unusual pressure dependence of the Co-Cl bond length. Instead the wave function obtained from the 3.2 GPa geometry exhibits some rather different donor-acceptor interactions than the three other wave functions. For the 3.2 GPa geometry wave function the central Co atom interacts with the terminal Cl atoms. The central Co atom acts as a donor and the Cl atoms as acceptors in donor-acceptor interactions with a significant stabilization energy (16.1 eV for alpha and 17.0 eV for beta). This suggests that the compression of the Cl-Co-Co-Co-Cl chain significantly increases the delocalization in the chain at 3.2 GPa.

Table S4. Donor-Acceptor Interactions between Cl and Co for which E(2) > 5 kcal/mol. The level of theory is B3LYP/6-311G**. The Co atoms next to Cl atoms in the Cl-Co-Co-Co-Cl chain are named *Co1*. The central Co atom is named *Co2*. P is the pressure under which the crystal structure used to extract the molecular geometry for the single point calculation is determined.

P [GPa]		Donor	NBO (i)	Acceptor NBO (j)		E(2) [kcal/mol]
0.0	α	LP(2)	Cl	LP*(6)	Co1	5.68
		LP(4)	Cl	LP*(6)	Co1	21.76
		LP*(6)	Co1	RY*(4)	Cl	5.73
		LP*(6)	Co1	RY*(5)	Cl	8.02
	β	LP(3)	Cl	LP*(6)	Co1	8.54
		LP(4)	Cl	LP*(5)	Co1	20.65
		LP(4)	Cl	LP*(6)	Co1	17.43
		LP*(6)	Co1	RY*(6)	Cl	6.71
		LP*(6)	Co1	RY*(8)	Cl	7.21
0.32(3)	α	LP(2)	Cl	LP*(6)	Co1	5.55
		LP(4)	Cl	LP*(6)	Co1	21.07
		LP*(6)	Co1	RY*(7)	Cl	10.32
	β	LP(3)	Cl	LP*(6)	Co1	8.48
		LP(4)	Cl	LP*(5)	Co1	19.18
		LP(4)	Cl	LP*(6)	Co1	17.75
		LP*(6)	Co1	RY*(6)	Cl	7.44
		LP*(6)	Co1	RY*(8)	Cl	8.58
0.74(4)	α	LP(2)	Cl	LP*(6)	Co1	5.58
		LP(4)	Cl	LP*(6)	Co1	21.56
		LP*(6)	Co1	RY*(6)	Cl	10.64
	β	LP(3)	Cl	LP*(6)	Co1	8.56
		LP(4)	Cl	LP*(5)	Co1	19.22
		LP(4)	Cl	LP*(6)	Co1	18.34
		LP*(6)	Co1	RY*(6)	Cl	7.63
		LP*(6)	Co1	RY*(8)	Cl	5.46
0.32(3)	α	LP(1)	Cl	LP*(6)	Co1	6.09
		LP(4)	Cl	LP*(6)	Co1	23.32
		LP*(6)	Co1	RY*(1)	Cl	9.36
		LP*(6)	Co1	RY*(7)	Cl	16.20
		LP*(6)	Co2	RY*(1)	Cl	10.63
	β	LP(4)	Cl	LP*(5)	Co1	20.29
		LP(4)	Cl	LP*(6)	Co1	20.94
		LP(3)	Cl	LP*(6)	Co1	8.65
		LP*(6)	Co1	Ry*(7)	Cl	14.66
		LP*(6)	Co2	RY*(7)	Cl	7.16

Table S5.The NBOs in table above: Dominating natural atomic orbitals (NAOs) (coefficient > 0.0999) in descending order from left to right, energy, occupancy and the amount of s, p and d character. The level of theory is B3LYP/6-311G**. The Co atoms next to Cl atoms in the Cl-Co-Co-Cl chain are named *Co1*. The central Co atom is named *Co2*. P is the pressure under which the crystal structure used to extract the molecular geometry for the single point calculation is determined.

P [GPa]		NE	80	Dominating NAOs	NBO	Occ.	s%	р%	d%
					energy				
					[eV]				
0.0	α	LP(2)	Cl	$3s > 3p_y > 3p_x$	-20.87	0.99	75.08	24.92	0.00
		LP(4)	Cl	$3p_y > 3s > 3p_x$	-11.25	0.96	24.24	75.73	0.03
		LP*(6)	Co1	4s	12.06	0.13	98.34	0.00	1.66
		RY*(4)	Cl		36.09	0.00	79.30	8.13	12.57
		RY*(5)	Cl		44.82	0.00	14.07	25.10	60.83
	β	LP(3)	Cl	$3s > 3p_y > 3p_x$	-23.84	0.99	91.05	8.95	0.00
		LP(4)	Cl	$3p_{y} > 3p_{x} > 3s$	-8.02	0.89	8.82	91.12	0.07
		LP*(5)	Co1	$3d_{xy} > 3d_z^2 > 3d_x^2 > 3d_{x-y}^2 > 4s$	-1.19	0.18	7.14	0.00	92.85
		LP*(6)	Co1	$4s > 3d_{xy} > 3d_{z}^{2}$	12.06	0.13	92.79	0.00	7.20
		Ry*(6)	Cl		47.61	0.00	87.34	5.94	6.72
		Ry*(8)	Cl		40.15	0.00	3.63	12.45	83.92
0.32(3)	α	LP(2)	Cl	$3s > 3p_y > 3p_z$	-20.36	0.99	73.04	26.96	0.00
		LP(4)	Cl	$3p_{y} > 3p_{x} > 3s$	-10.76	0.96	22.13	77.84	0.03
		LP*(6)	Co1	4s	12.79	0.13	98.22	0.00	1.78
		RY*(7)	Cl		46.80	0.00	98.36	1.59	0.05
	β	LP(3)	Cl	$3s > 3p_v > 3p_v$	-23.81	0.99	91.59	8.41	0.00
	•	LP(4)	Cl	$3p_v > 3p_x > 3s$	-7.82	0.89	8.20	91.74	0.07
		LP*(5)	Co1	$3d_{yy} > 3d_z^2 > 3d_y^2 > 3d_y^2 > 4s$	-1.44	0.18	5.46	0.00	94.53
		LP*(6)	Co1	$4s > 3d_{yy} > 3d_{y}^{2}$	12.61	0.13	94.47	0.00	5.52
		RY*(6)	Cl	XY 2	47.24	0.00	86.66	6.05	7.28
		RY*(8)	Cl		41.08	0.00	4.05	11.64	84.31
0.74(4)	α	LP(2)	Cl	$3s > 3p_{y} > 3p_{z} > 3p_{z}$	-20.64	0.99	74.48	25.52	0.00
- ()		LP(4)	Cl	$3p_v > 3p_v > 3s$	-10.85	0.96	22.64	77.33	0.03
		LP*(6)	Co1	4s	13.37	0.13	98.23	0.00	1.76
		RY*(6)	Cl		46.06	0.00	96.21	3.52	0.28
	ß	LP(3)	Cl	$3s > 3p_v > 3p_v$	-23.77	0.99	91.38	8.62	0.00
	F	LP(4)	CI	$3p_{y} > 3p_{y} > 3s$	-7.85	0.89	8.35	91.59	0.06
		LP*(5)	Co1	$3d_{yy} > 3d_y^2 > 3d_y^2 > 2d_y^2 > 4s$	-1.39	0.19	5.15	0.00	94.84
		LP*(6)	Co1	$4s > 3d_{y} > 3d_{z}^{2}$	13.18	0.13	94.81	0.00	5.18
		RY*(6)	Cl		47.72	0.00	89.41	2.04	8.55
		RY*(8)	Cl		32.83	0.00	2.82	5.13	92.05
3,32(3)	α	IP(1)	Cl	3s > 3n > 3n > 3n > 3n	-20.64	0.99	74.75	25.25	0.00
0.02(0)		LP(4)	Cl	$3n_{1} > 3n_{2} > 3s_{3}$	-10.60	0.95	21.51	78.46	0.03
		LP*(6)	Co1	<u>4</u> s	15.63	0.14	98.21	0.00	1 79
		LP*(6)	Co2	$4s > 3d_{y} > 3d_{z}^{2} > 3d_{y}^{2}$	16.08	0.15	88.29	0.00	11 71
		RY*(1)	CI	$4n_{x} > 4n_{y} > 3d_{y} > 3d_{z}^{2} > 3d_{y}^{2} > 2d_{y}^{2}$	17.18	0.00	0.13	68.96	30.91
		RY*(7)			51.00	0.00	86 51	7 47	6.03
	ß	I P(2)		3s > 3n > 03n	-21.67	0.00	80.68	19.37	0.05
	Ч	I P(A)		3n > 3n > 3c	-7 87	0.33	8 22	91.60	0.00
		LI (+)		$3p_{y} - 3p_{x} - 35$	-1 5/	0.00	2 /6	0.01	96 52
		LF (J)		$3u_{XY} > 3u_Z > 43$	-1.J4 15 E4	0.20	06.40	0.01	2 50.33
		LP (0)	Co2	$45 \times 3u_{XY} \times 3u_{Z}$	17.01	0.13	90.49	0.01	5.50
		LP (0)		45 > 30 _{xy} > 30 _z	17.01	0.15	93.33	0.00	4.07
		KY*(/)	U U	1	53.09	0.00	82.78	3.55	13.67

Supporting information – Hirshfeld surface analysis

CrystalExplorer was used to calculate Hirshfeld surfaces, plot d_{norm} on the surfaces (range from -0.5 to 1.2) and plot fingerprints. Hirshfeld surface resolution was set to High (standard).^{24,25} Expanded fingerprint plots are shown in order to include the entire (d_{i} , d_{e}) range of the data.











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