

Bis(2-chloro-*N,N*-dimethylethan-1-aminium) tetrachloridocobaltate(II) and tetrachloridozincate(II)

Katelyn McGinness, Kim Minton, Katelyn White and Marcus R. Bond*

Department of Chemistry and Physics, Southeast Missouri State University, Cape Girardeau, MO 63701, USA. *Correspondence e-mail: mbond@semo.edu

Received 9 April 2024

Accepted 30 April 2024

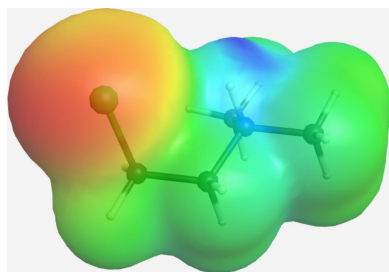
Edited by S. P. Kelley, University of Missouri-Columbia, USA

Keywords: crystal structure; *gauche* effect; DFT calculation; disorder; molecular switch.**CCDC references:** 2352359; 2352358**Supporting information:** this article has supporting information at journals.iucr.org/e

The few examples of structures containing the 2-chloro-*N,N*-dimethylethan-1-aminium or 3-chloro-*N,N*-dimethylpropan-1-aminium cations show a competition between *gauche* and *anti* conformations for the chloroalkyl chain. To explore further the conformational landscape of these cations, and their possible use as molecular switches, the title salts, $(C_4H_{11}ClN)_2[CoCl_4]$ and $(C_4H_{11}ClN)_2[ZnCl_4]$, were prepared and structurally characterized. Details of both structures are in close agreement. The inorganic complex exhibits a slightly flattened tetrahedral geometry that likely arises from bifurcated N–H hydrogen bonds from the organic cations. The alkyl chain of the cation is disordered between *gauche* and *anti* conformations with the *gauche* conformation occupancy refined to 0.707 (2) for the cobaltate. The *gauche* conformation places the terminal Cl atom at a tetrahedral face of the inorganic complex with a contact distance of 3.7576 (9) Å to the Co^{2+} center. The *anti* conformation places the terminal Cl atom at a contact distance to a neighboring *anti* conformation terminal Cl atom that is ~ 1 Å less than the sum of the van der Waals radii. Thus, if the *anti* conformation is present at a site, then the nearest neighbor must be *gauche*. DFT geometry optimizations indicate the *gauche* conformation is more stable *in vacuo* by 0.226 eV, which reduces to 0.0584 eV when calculated in a uniform dielectric. DFT geometry optimizations for the unprotonated molecule indicate the *anti* conformation is stabilized by 0.0428 eV *in vacuo*, with no strongly preferred conformation in uniform dielectric, to provide support to the notion that this cation could function as a molecular switch *via* deprotonation.

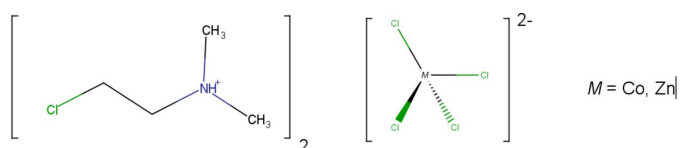
1. Chemical context

The recently published structure of 3-chloro-*N,N*-dimethylpropan-1-aminium chloride reported the conformation of the molecular cation (henceforth 3CLPA⁺) as *gauche* for the terminal Cl atom (Bond & Silwal, 2023). DFT geometry optimizations *in vacuo* indicate that the *gauche* conformation is more stable than *anti* for the molecular cation, as well as for the 2-chloro-*N,N*-dimethylethan-1-aminium analog (henceforth 2CLEA⁺). In both cases the molecular cations appear to exhibit the *gauche* effect in which the bonding pair of a C–H bond β to the terminal halogen atom of the chain is donated to the antibonding orbital of the C–X bond ($X = \text{halogen}$) to stabilize the *gauche* conformation through hyperconjugation (Wolfe, 1972). A recent computational study of 1,2-dihaloethanes reports that this stabilization due to hyperconjugation is always present, but other energy contributions – such as steric interactions – are more important so that the *gauche* effect is typically observed only with fluorine (Rodrigues Silva *et al.*, 2021). However, in the 3CLPA⁺ and 2CLEA⁺ cations the terminal Cl atom is closer to the formal center of positive



charge when in the *gauche* conformation, which may provide an additional contribution to energetic stability.

We are interested in investigating the competition between *gauche* and *anti* conformations for these molecular cations in different chemical environments in order to explore their possible use as molecular switches. If the *gauche* conformation is stabilized by interaction with the positive charge center in the cation, then it is possible with loss of this interaction through deprotonation that the *anti* conformation becomes more stable and would allow for a change in conformation by altering the degree of protonation. Here we report the structures of 2CLEA^+ with the tetrahedral complex anions CoCl_4^{2-} and ZnCl_4^{2-} .



2. Structural commentary

The structures are isomorphous with unit-cell parameters in close agreement, *e.g.* unit-cell volumes agree within 2 s.u. Both tetrahedral complexes occupy sites of twofold rotational symmetry with a slight flattening about the twofold axis to produce some $\text{Cl}-M-\text{Cl}$ ($M = \text{Co}, \text{Zn}$) angles greater than 109.5° . $M-\text{Cl}$ bond lengths range from 2.25–2.29 Å, in good agreement with average bond lengths of 2.27 (2) Å for CoCl_4^{2-} and 2.27 (4) Å for ZnCl_4^{2-} calculated from structures in the Cambridge Structural Database [512 and 960 hits, respectively; version 5.45 (November, 2023); Groom *et al.* (2016)].

Of greater interest is the organic cation, which exhibits disorder between the *gauche* [s.o.f = 0.707 (2) for CoCl_4^{2-} and

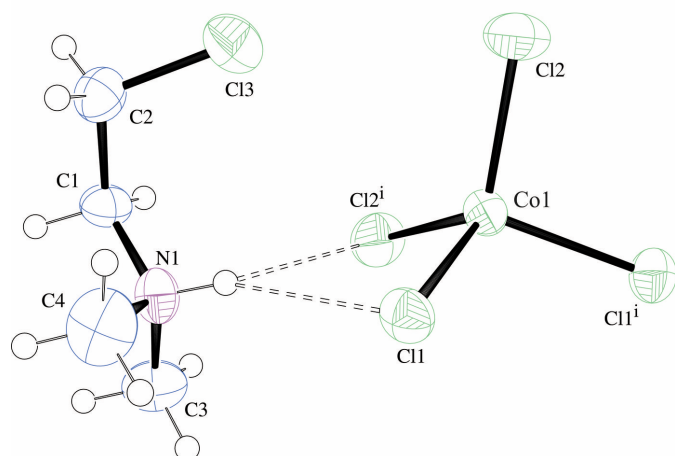


Figure 1

Displacement ellipsoid plot (50% level) of the organic cation and complex anion in $(2\text{CLEA}^+)_2\text{CoCl}_4$ with labels for non-H atoms. The *gauche* conformation of the organic cation only is shown. H atoms are drawn as circles of arbitrary radii and $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonding is represented by dashed lines.

Table 1

Selected geometric parameters (Å, °) for cobaltate.

Co1–Cl1	2.2873 (6)	N1–C1	1.509 (5)
Co1–Cl2	2.2618 (6)	C1–C2	1.534 (6)
N1–C3	1.482 (3)	C2–Cl3	1.776 (3)
N1–C4	1.483 (3)		
Cl1 ⁱ –Co1–Cl1	111.86 (3)	C3–N1–C1	105.4 (3)
Cl1–Co1–Cl2	108.17 (2)	C4–N1–C1	114.8 (4)
Cl1–Co1–Cl2 ⁱ	104.58 (2)	N1–C1–C2	116.2 (5)
Cl2 ⁱ –Co1–Cl2	119.62 (4)	C1–C2–Cl3	111.0 (4)
C3–N1–C4	110.6 (2)		

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

Table 2

Selected geometric parameters (Å, °) for zincate.

Zn1–Cl2	2.2553 (5)	N1–C4	1.485 (3)
Zn1–Cl1	2.2883 (5)	N1–C1	1.515 (5)
N1–ClA	1.476 (9)	C1–C2	1.535 (5)
N1–C3	1.480 (3)	C2–Cl3	1.779 (3)
Cl2–Zn1–Cl2 ⁱ	118.93 (3)	C3–N1–C4	110.5 (2)
Cl2–Zn1–Cl1 ⁱ	104.94 (2)	C3–N1–C1	105.3 (2)
Cl2–Zn1–Cl1	108.36 (2)	C4–N1–C1	114.6 (3)
Cl1 ⁱ –Zn1–Cl1	111.38 (3)	N1–C1–C2	116.3 (4)
Cl1A–N1–C3	119.8 (5)	C1–C2–Cl3	110.7 (3)
Cl1A–N1–C4	111.1 (8)		

0.697 (2) for ZnCl_4^{2-}] and *anti* conformations (the dimethylammonium head group is ordered). The $\text{N1}-\text{C1}-\text{C2}-\text{Cl3}$ torsion angles are $61.6 (7)^\circ$ in the CoCl_4^{2-} and $-61.3 (6)^\circ$ in the ZnCl_4^{2-} salts for the *gauche* conformation and, likewise, $-179.7 (13)$ and $179.3 (9)^\circ$, respectively, for the *anti*. Bond lengths and angles within the cation correspond to expected values, disregarding small distortions that arise due to refinement of atoms of the disordered pair in close proximity. Displacement ellipsoid plots with labels for non-H atoms are presented in Fig. 1 for the CoCl_4^{2-} salt showing only the *gauche* conformation of the organic cation, and in Fig. 2 for the ZnCl_4^{2-} salt showing only the *anti* conformation. Bond

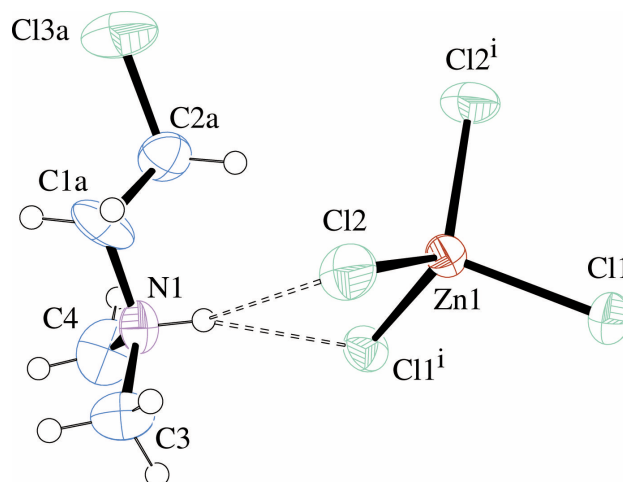


Figure 2

Displacement ellipsoid plot (50% level) of the organic cation and complex anion in $(2\text{CLEA}^+)_2\text{ZnCl}_4$ with labels for non-H atoms. The *anti* conformation of the organic cation only is shown. H atoms are drawn as circles of arbitrary radii and $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonding is represented by dashed lines.

Table 3
Hydrogen-bond geometry (Å, °) for cobaltate.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1\cdots Cl1$	0.87 (3)	2.51 (3)	3.3093 (19)	152 (2)
$N1-H1\cdots Cl2^i$	0.87 (3)	3.02 (3)	3.564 (2)	122 (2)

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

lengths and angles for non-H atoms are presented in Table 1 for the $CoCl_4^{2-}$ salt, with only the *gauche* conformation values, and in Table 2 for the $ZnCl_4^{2-}$ salt, with only the *anti* conformation values.

DFT geometry optimizations [B3LYP, 6311+G(d,p); GAMESS (Schmidt *et al.*, 1993)] *in vacuo* of 2CLEA⁺ yield an energy for the *gauche* conformation that is 0.226 eV less than the *anti* conformation for a 52.737° N–C–C–Cl torsion angle (0.228 eV less for a torsion angle of –52.738°). To approximate the ionic environment of the cation in the crystal, the optimizations were performed in a uniform dielectric constant of 78.4. This results in a reduction of *gauche* conformation stabilization to 0.0584 eV (torsion angle = 59.1°; by 0.0582 eV for torsion angle = –58.785°), but yields better agreement with observed torsion angle values. [Optimized torsion angles for the *anti* conformation with magnitudes of 173.858° (*in vacuo*) and 173.819° (dielectric) deviate slightly from observed values.] Similar optimizations for the unprotonated molecule show both *gauche* conformations are destabilized *in vacuo* (by 0.0412 eV for torsion angle = 66.377° and by 0.0428 eV for torsion angle = –64.735°). Energy differences for optimizations performed in uniform dielectric for the unprotonated molecule are not as stark: *gauche* conformations are slightly stabilized by 0.00792 eV (–65.149°) or 0.00624 eV (64.459°). These results show promise of a switch from *gauche* to *anti* *via* deprotonation. An electrostatic potential plot of the *gauche* conformation from the uniform dielectric calculation is presented in Fig. 3.

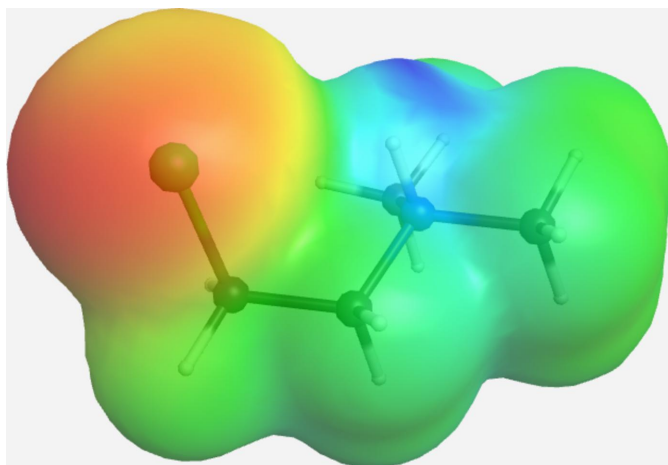


Figure 3
Electrostatic potential plot of the 2CLEA⁺ cation calculated in uniform dielectric for the *gauche* conformation with a ball-and-stick model of the optimized geometry shown within the electron density envelope. Red indicates regions of negative charge accumulation and blue regions of positive charge.

Table 4
Hydrogen-bond geometry (Å, °) for zincate.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1\cdots Cl1^i$	0.87 (3)	2.51 (3)	3.3124 (18)	156 (2)
$N1-H1\cdots Cl2$	0.87 (3)	3.03 (3)	3.5620 (19)	121 (2)

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

3. Supramolecular features

The dimethylammonium headgroup forms an asymmetric, bifurcated hydrogen bond to Cl1 and Cl2 resulting in the most acute Cl–M–Cl angle in the complex anion – and a likely origin for the observed tetrahedral flattening. Hydrogen-bond lengths and angles are presented in Tables 3 and 4 for the $CoCl_4^{2-}$ and $ZnCl_4^{2-}$ salts, respectively.

In the *gauche* conformation of the molecular cation, the terminal Cl atom is placed slightly offset from the center of the tetrahedral face defined by Cl1, Cl2, and Cl2ⁱ [symmetry code: (i) $1 - x, y, \frac{1}{2} - z$]. This places the terminal Cl atom at a distance of 3.7576 (9) Å from the Co²⁺ center [3.7690 (10) Å for Zn²⁺] with the shortest Clⁱ⋯Cl contact distance [Cl2ⁱ⋯Cl3 = 3.4293 (11) Å for $CoCl_4^{2-}$; 3.4237 (11) Å for $ZnCl_4^{2-}$] slightly less than 3.50 Å – the sum of the van der Waals radii. In the *anti* conformation, a methylene H atom from the carbon α to the terminal Cl atom is instead directed at this face and forms contact distances of 3.2–3.3 Å to the Cl atoms. Meanwhile, the terminal Cl atom now forms a short contact [Cl3Aⁱⁱ⋯Cl3Aⁱⁱⁱ = 2.588 (4) Å, Cl3Aⁱⁱ⋯Cl3Aⁱⁱⁱ = 2.568 (4) Å; symmetry codes: (ii) $\frac{3}{2} - x, \frac{1}{2} - y, 1 - z$, for $CoCl_4^{2-}$; (iii) $\frac{1}{2} - x, \frac{5}{2} - y, -z$, for $ZnCl_4^{2-}$] with a terminal *anti* conformation Cl atom in the nearest neighbor that is ~1 Å less than the sum of the van der Waals radii. Hence, any *anti* conformation molecular cation must have a *gauche* conformation cation as a nearest neighbor. This provides another driver for the dominance of the *gauche* conformation in these structures.

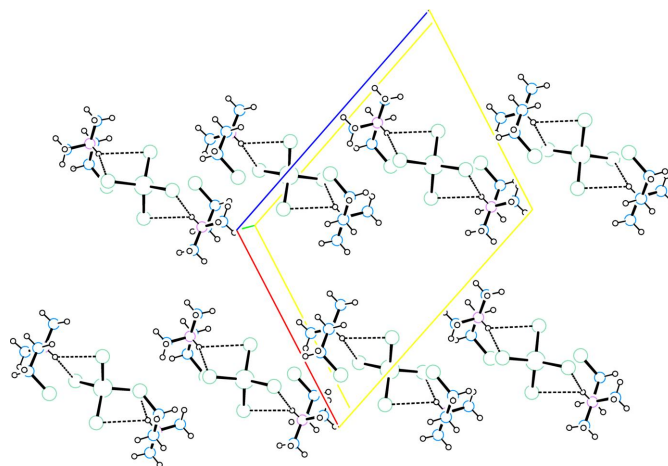


Figure 4
Layer packing diagram viewed down the b axis for $(2CLEA^+)_2CoCl_4$ (*gauche* conformation only) that depicts portions of two rows of formula units along (101) that form a layer in the ac plane. The a axis slants down and to the right, the c axis slants up and to the right. Atoms are drawn as circles of arbitrary radii and N–H⋯Cl hydrogen bonding is represented by dashed lines

Table 5
Experimental details.

	Cobaltate	Zincate
Crystal data		
Chemical formula	(C ₄ H ₁₁ CIN) ₂ [CoCl ₄]	(C ₄ H ₁₁ CIN) ₂ [ZnCl ₄]
<i>M_r</i>	417.93	424.34
Crystal system, space group	Monoclinic, <i>C2/c</i>	Monoclinic, <i>C2/c</i>
Temperature (K)	295	295
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.7521 (6), 8.9648 (4), 16.6801 (10)	12.7297 (7), 8.9784 (5), 16.6837 (11)
β (°)	111.057 (1)	111.062 (2)
<i>V</i> (Å ³)	1779.53 (16)	1779.43 (18)
<i>Z</i>	4	4
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	1.85	2.26
Crystal size (mm)	0.30 × 0.27 × 0.26	0.39 × 0.38 × 0.29
Data collection		
Diffractometer	Bruker D8 Quest Eco	Bruker D8 Quest Eco
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.696, 0.746	0.472, 0.560
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	23748, 2041, 1676	46381, 2843, 2479
<i>R</i> _{int}	0.042	0.036
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.650	0.725
Refinement		
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.030, 0.064, 1.09	0.033, 0.070, 1.12
No. of reflections	2041	2843
No. of parameters	113	113
No. of restraints	1	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.38, -0.29	0.57, -0.40

Computer programs: *APEX3* and *SAINT* (Bruker, 2017), *SHELXT2018/2* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick 2015b), *ORTEP-3 for Windows* (Farrugia, 2012) and *pubCIF* (Westrip, 2010).

The three-dimensional packing can be described starting with parallel rows of hydrogen-bonded formula units along (101) arranged into layers in the *ac* plane, as shown in the layer packing diagram of Fig. 4. Rows in neighboring layers nest between the rows of a given layer, with neighboring layers related by the *C*-centering translation, as shown in the unit-cell packing diagram of Fig. 5.

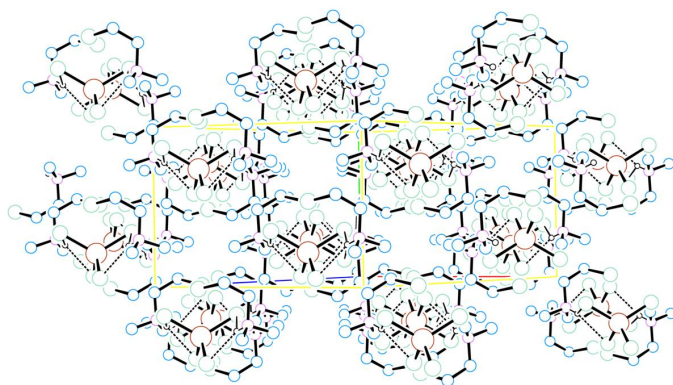


Figure 5
Unit-cell packing diagram for (2CLEA⁺)₂ZnCl₄ viewed down (101) showing the stacking of four of the layers presented in Fig. 4 with the *b* axis vertical. H atoms are omitted for clarity (except for N–H), atoms are drawn as circles of arbitrary radii, and N–H...Cl hydrogen bonding is represented by dashed lines.

4. Database survey

Structural results for 2CLEA⁺ or 3CLPA⁺ cations have been sparsely reported. A survey of the Cambridge Structural Database (version 5.45, November, 2023; Groom *et al.*, 2016) yields only two known prior examples of structures containing 2CLEA⁺: an (Mo₂O₂Cl₈)²⁻ salt (CSD refcode POSWAX; Marchetti *et al.*, 2015), in which the *gauche* conformation is found, and a chloride salt (CSD refcode: URORUR; Muller *et al.*, 2021) where the *anti* conformation is found, albeit with a disordered alkyl chain. For 3CLPA⁺, besides the aforementioned chloride salt there is one other structure containing 3-chloro-*N,N*-propan-1-amine as a ligand in a di(μ -hydrido) dialuminium complex (CSD refcode: NIGGOZ; Andrews *et al.*, 1997) where the *gauche* conformation is also found. No structures containing the unprotonated or uncoordinated molecules have been reported. There are also no reported structures for the longer chain chlorobutyl or chloropentyl analogs.

5. Synthesis and crystallization

Both compounds were prepared by dissolving 2-chloro-*N,N*-dimethylethan-1-amium chloride with 1.00 g of CoCl₂·6H₂O or ZnCl₂ in a 2:1 molar ratio in water. The solutions were acidified with concentrated HCl(aq) to yield ~6 *M* HCl and produce a definite blue color in the cobalt(II) solution. The solutions were evaporated to a syrup with the syrup redis-

solved in ethanol to yield crystals of the title compounds upon further evaporation.

6. Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 5. For both compounds, initial structure solution identified positions of all non-H atoms except those of the *anti* conformation. Prominent electron density difference map peaks then identified atoms of the *anti* conformation. Common site occupation factors for each conformation were refined with the constraint that their sum equal 1.0. H-atom positions were visible on the electron density difference map, but were calculated and refined using a riding model for those bound to C with isotropic displacement parameters set to 1.2 or $1.5 \times U_{iso}$ of the parent atom for methylene or methyl H atoms, respectively. The H atom bound to N was freely refined to a reasonable N–H bond length and the N1–C1A distance was constrained to a chemically reasonable distance (1.50 ± 0.01 Å) using the DFIX command in *SHELX*.

Low angle reflections (four for CoCl_4^{2-} and one for ZnCl_4^{2-} salts) with $F_o^2 \ll F_c^2$ were assumed to be blocked by the beam catcher and were omitted from the refinement. For the ZnCl_4^{2-} structure, *APEX3* control software suggested a data-collection strategy to $\theta_{max} = 36^\circ$. However data analysis (*WinGX 2021.3*; Farrugia, 2012) indicated $\langle I/\sigma \rangle$ less than 2.0 for reflections beyond $\theta = 30.6^\circ$. Thus reflection data beyond $\theta = 31^\circ$ were omitted from the final refinement.

Acknowledgements

The authors thank Ms Annette Drury for assistance in preparation of the ZnCl_4^{2-} salt.

References

- Andrews, P. C., Gardiner, M. G., Raston, C. L. & Tolhurst, V.-A. (1997). *Inorg. Chim. Acta*, **259**, 249–255.
- Bond, M. R. & Silwal, S. (2023). *IUCrData*, **8**, x230015.
- Bruker (2017). *APEX3* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.
- Marchetti, F., Pampaloni, G. & Zacchini, S. (2015). *Polyhedron*, **85**, 369–375.
- Muller, K., Hosten, E. C. & Betz, R. (2021). *Z. Kristallogr. New Cryst. Struct.* **236**, 287–289.
- Rodrigues Silva, D., de Azevedo Santos, L., Hamlin, T. A., Fonseca Guerra, C., Freitas, M. P. & Bickelhaupt, F. M. (2021). *ChemPhysChem*, **22**, 641–648.
- Schmidt, M. W., Baldrige, K. K., Boatz, J. A., Elbert, S. T., Gordon, M. S., Jensen, J. H., Koseki, S., Matsunaga, N., Nguyen, K. A., Su, S., Windus, T. L., Dupuis, M. & Montgomery, J. A. (1993). *J. Comput. Chem.* **14**, 1347–1363.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Wolfe, S. (1972). *Acc. Chem. Res.* **5**, 102–111.

supporting information

Acta Cryst. (2024). E80 [https://doi.org/10.1107/S2056989024003955]

Bis(2-chloro-*N,N*-dimethylethan-1-aminium) tetrachloridocobaltate(II) and tetrachloridozincate(II)

Katelyn McGinness, Kim Minton, Katelyn White and Marcus R. Bond

Computing details

Bis(2-chloro-*N,N*-dimethylethan-1-aminium) tetrachloridocobaltate(II) (cobaltate)

Crystal data

(C₄H₁₁ClN)₂[CoCl₄]
 $M_r = 417.93$
 Monoclinic, *C2/c*
 Hall symbol: -C 2yc
 $a = 12.7521$ (6) Å
 $b = 8.9648$ (4) Å
 $c = 16.6801$ (10) Å
 $\beta = 111.057$ (1)°
 $V = 1779.53$ (16) Å³
 $Z = 4$

$F(000) = 852$
 $D_x = 1.56$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 9986 reflections
 $\theta = 2.9$ – 27.4 °
 $\mu = 1.85$ mm⁻¹
 $T = 295$ K
 Gem, blue
 0.30 × 0.27 × 0.26 mm

Data collection

Bruker D8 Quest Eco
 diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Krause *et al.*, 2015)
 $T_{\min} = 0.696$, $T_{\max} = 0.746$
 23748 measured reflections

2041 independent reflections
 1676 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.042$
 $\theta_{\max} = 27.5$ °, $\theta_{\min} = 3.4$ °
 $h = -16 \rightarrow 16$
 $k = -11 \rightarrow 11$
 $l = -21 \rightarrow 21$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.030$
 $wR(F^2) = 0.064$
 $S = 1.09$
 2041 reflections
 113 parameters
 1 restraint
 Primary atom site location: dual
 Hydrogen site location: mixed

H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0202P)^2 + 2.2595P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.38$ e Å⁻³
 $\Delta\rho_{\min} = -0.29$ e Å⁻³
 Extinction correction: *SHELXL2018/3*
 (Sheldrick 2015b)
 Extinction coefficient: 0.0038 (3)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Co1	0.5	0.77754 (4)	0.25	0.03399 (13)	
Cl1	0.63314 (4)	0.92047 (6)	0.34886 (3)	0.04269 (15)	
Cl2	0.40423 (5)	0.65066 (7)	0.31892 (4)	0.05376 (18)	
N1	0.84438 (16)	0.6926 (2)	0.36634 (12)	0.0402 (4)	
H1	0.775 (2)	0.725 (3)	0.3517 (17)	0.066 (8)*	
C1	0.8515 (7)	0.5245 (5)	0.3673 (6)	0.0395 (13)	0.707 (2)
H1A	0.929586	0.496545	0.381431	0.047*	0.707 (2)
H1B	0.810217	0.488369	0.309775	0.047*	0.707 (2)
C2	0.8069 (3)	0.4440 (4)	0.4297 (2)	0.0465 (8)	0.707 (2)
H2A	0.848364	0.477204	0.487909	0.056*	0.707 (2)
H2B	0.818475	0.337488	0.427118	0.056*	0.707 (2)
Cl3	0.66156 (8)	0.48055 (11)	0.40385 (6)	0.0581 (3)	0.707 (2)
C1A	0.8273 (19)	0.5310 (12)	0.3788 (17)	0.055 (5)	0.293 (2)
H1AA	0.800336	0.479291	0.324113	0.066*	0.293 (2)
H1AB	0.897006	0.48509	0.415285	0.066*	0.293 (2)
C2A	0.7424 (9)	0.5258 (10)	0.4203 (6)	0.051 (2)	0.293 (2)
H2AA	0.672082	0.570241	0.383851	0.061*	0.293 (2)
H2AB	0.768918	0.576965	0.475201	0.061*	0.293 (2)
Cl3A	0.7270 (3)	0.3331 (3)	0.43356 (19)	0.0799 (11)	0.293 (2)
C3	0.8885 (2)	0.7413 (3)	0.29966 (17)	0.0572 (7)	
H3A	0.885462	0.848115	0.295397	0.086*	
H3B	0.843773	0.698591	0.245341	0.086*	
H3C	0.964987	0.708767	0.315027	0.086*	
C4	0.9070 (3)	0.7654 (3)	0.44973 (17)	0.0687 (8)	
H4A	0.984779	0.737603	0.468255	0.103*	
H4B	0.876356	0.733971	0.491816	0.103*	
H4C	0.900302	0.871732	0.443083	0.103*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Co1	0.0301 (2)	0.0362 (2)	0.0354 (2)	0	0.01147 (16)	0
Cl1	0.0383 (3)	0.0475 (3)	0.0375 (3)	-0.0055 (2)	0.0078 (2)	-0.0033 (2)
Cl2	0.0611 (4)	0.0447 (3)	0.0666 (4)	-0.0097 (3)	0.0364 (3)	0.0013 (3)
N1	0.0339 (9)	0.0456 (11)	0.0413 (10)	0.0079 (8)	0.0137 (8)	-0.0021 (8)
C1	0.043 (4)	0.040 (2)	0.042 (3)	-0.0033 (16)	0.023 (2)	0.0027 (16)
C2	0.0492 (19)	0.0449 (19)	0.0467 (19)	0.0064 (16)	0.0188 (15)	0.0019 (16)
Cl3	0.0479 (6)	0.0665 (6)	0.0663 (6)	-0.0018 (4)	0.0280 (4)	-0.0007 (5)
C1A	0.038 (9)	0.086 (10)	0.047 (9)	-0.015 (6)	0.024 (5)	0.001 (6)

C2A	0.062 (6)	0.047 (5)	0.048 (5)	0.004 (5)	0.025 (4)	0.009 (4)
Cl3A	0.113 (2)	0.0584 (16)	0.0850 (19)	-0.0153 (14)	0.0554 (17)	0.0128 (13)
C3	0.0704 (17)	0.0520 (15)	0.0552 (15)	-0.0085 (13)	0.0297 (13)	0.0012 (12)
C4	0.081 (2)	0.0703 (19)	0.0485 (15)	0.0016 (15)	0.0150 (14)	-0.0161 (14)

Geometric parameters (Å, °)

Co1—C11	2.2873 (6)	C1—H1B	0.97
Co1—C12	2.2618 (6)	C1—C2	1.534 (6)
N1—C3	1.482 (3)	C2—H2A	0.97
C3—H3A	0.96	C2—H2B	0.97
C3—H3B	0.96	C2—C13	1.776 (3)
C3—H3C	0.96	N1—C1A	1.490 (10)
N1—C4	1.483 (3)	C1A—H1AA	0.97
C4—H4A	0.96	C1A—H1AB	0.97
C4—H4B	0.96	C1A—C2A	1.480 (15)
C4—H4C	0.96	C2A—H2AA	0.97
N1—H1	0.87 (3)	C2A—H2AB	0.97
N1—C1	1.509 (5)	C2A—Cl3A	1.762 (9)
C1—H1A	0.97		
C11 ⁱ —Co1—C11	111.86 (3)	C2—C1—H1A	108.2
C11—Co1—C12	108.17 (2)	N1—C1—H1B	108.2
C11—Co1—C12 ⁱ	104.58 (2)	C2—C1—H1B	108.2
C12 ⁱ —Co1—C12	119.62 (4)	H1A—C1—H1B	107.4
C3—N1—C4	110.6 (2)	C1—C2—C13	111.0 (4)
N1—C3—H3A	109.5	C1—C2—H2A	109.4
N1—C3—H3B	109.5	Cl3—C2—H2A	109.4
H3A—C3—H3B	109.5	C1—C2—H2B	109.4
N1—C3—H3C	109.5	Cl3—C2—H2B	109.4
H3A—C3—H3C	109.5	H2A—C2—H2B	108
H3B—C3—H3C	109.5	C3—N1—C1A	120.4 (7)
N1—C4—H4A	109.5	C4—N1—C1A	110.7 (11)
N1—C4—H4B	109.5	C2A—C1A—N1	105.3 (9)
H4A—C4—H4B	109.5	C2A—C1A—H1AA	110.7
N1—C4—H4C	109.5	N1—C1A—H1AA	110.7
H4A—C4—H4C	109.5	C2A—C1A—H1AB	110.7
H4B—C4—H4C	109.5	N1—C1A—H1AB	110.7
C3—N1—C1	105.4 (3)	H1AA—C1A—H1AB	108.8
C4—N1—C1	114.8 (4)	C1A—C2A—Cl3A	102.9 (7)
C3—N1—H1	108.0 (18)	C1A—C2A—H2AA	111.2
C4—N1—H1	105.3 (18)	Cl3A—C2A—H2AA	111.2
C1A—N1—H1	100 (2)	C1A—C2A—H2AB	111.2
C1—N1—H1	112.6 (19)	Cl3A—C2A—H2AB	111.2
N1—C1—C2	116.2 (5)	H2AA—C2A—H2AB	109.1
N1—C1—H1A	108.2		
C3—N1—C1—C2	-178.1 (5)	C3—N1—C1A—C2A	-156.9 (10)

C4—N1—C1—C2	59.9 (7)	C4—N1—C1A—C2A	71.9 (16)
N1—C1—C2—Cl3	61.6 (7)	N1—C1A—C2A—Cl3A	-179.7 (13)

Symmetry code: (i) $-x+1, y, -z+1/2$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots Cl1	0.87 (3)	2.51 (3)	3.3093 (19)	152 (2)
N1—H1 \cdots Cl2 ⁱ	0.87 (3)	3.02 (3)	3.564 (2)	122 (2)

Symmetry code: (i) $-x+1, y, -z+1/2$.

Bis(2-chloro-*N,N*-dimethylethan-1-aminium) tetrachloridozincate(II) (zincate)

Crystal data

(C₄H₁₁ClN)₂[ZnCl₄]
 $M_r = 424.34$
 Monoclinic, $C2/c$
 Hall symbol: $-C 2yc$
 $a = 12.7297$ (7) \AA
 $b = 8.9784$ (5) \AA
 $c = 16.6837$ (11) \AA
 $\beta = 111.062$ (2) $^\circ$
 $V = 1779.43$ (18) \AA^3
 $Z = 4$

$F(000) = 864$
 $D_x = 1.584$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA
 Cell parameters from 9979 reflections
 $\theta = 2.8\text{--}33.7^\circ$
 $\mu = 2.26$ mm⁻¹
 $T = 295$ K
 Irregular, colourless
 $0.39 \times 0.38 \times 0.29$ mm

Data collection

Bruker D8 Quest Eco
 diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Krause *et al.*, 2015)
 $T_{\min} = 0.472$, $T_{\max} = 0.560$
 46381 measured reflections

2843 independent reflections
 2479 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.036$
 $\theta_{\max} = 31.0^\circ$, $\theta_{\min} = 3.4^\circ$
 $h = -18 \rightarrow 18$
 $k = -12 \rightarrow 12$
 $l = -24 \rightarrow 24$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.070$
 $S = 1.12$
 2843 reflections
 113 parameters
 1 restraint
 Primary atom site location: dual
 Hydrogen site location: mixed

H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0155P)^2 + 3.2372P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.57$ e \AA^{-3}
 $\Delta\rho_{\min} = -0.40$ e \AA^{-3}
 Extinction correction: *SHELXL2018/3*
 (Sheldrick 2015b)
 Extinction coefficient: 0.0035 (3)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Zn1	0.5	0.72176 (4)	0.25	0.03333 (10)	
Cl1	0.63307 (4)	0.57810 (6)	0.34859 (3)	0.04085 (12)	
Cl2	0.40494 (5)	0.84939 (6)	0.31868 (4)	0.05219 (15)	
N1	0.15576 (15)	0.8071 (2)	0.13379 (11)	0.0396 (4)	
H1	0.223 (2)	0.770 (3)	0.1486 (17)	0.055 (7)*	
C1	0.1482 (5)	0.9756 (5)	0.1328 (5)	0.0393 (10)	0.697 (2)
H1A	0.189643	1.011624	0.190345	0.047*	0.697 (2)
H1B	0.069934	1.003059	0.118912	0.047*	0.697 (2)
C2	0.1923 (3)	1.0567 (4)	0.0703 (2)	0.0451 (7)	0.697 (2)
H2A	0.180985	1.163084	0.073337	0.054*	0.697 (2)
H2B	0.15046	1.024182	0.012066	0.054*	0.697 (2)
Cl3	0.33801 (8)	1.01959 (11)	0.09585 (6)	0.0569 (3)	0.697 (2)
C1A	0.1726 (14)	0.9672 (11)	0.1224 (12)	0.052 (4)	0.303 (2)
H1C	0.200388	1.01761	0.177512	0.063*	0.303 (2)
H1D	0.102578	1.01361	0.086803	0.063*	0.303 (2)
C2A	0.2568 (7)	0.9742 (9)	0.0801 (5)	0.0480 (18)	0.303 (2)
H2C	0.229594	0.923437	0.025068	0.058*	0.303 (2)
H2D	0.32746	0.929578	0.115896	0.058*	0.303 (2)
Cl3A	0.2728 (3)	1.1668 (3)	0.06669 (18)	0.0773 (9)	0.303 (2)
C3	0.1113 (2)	0.7582 (3)	0.20017 (16)	0.0552 (6)	
H3A	0.034943	0.791657	0.185019	0.083*	
H3B	0.156482	0.799774	0.254694	0.083*	
H3C	0.113532	0.65148	0.203863	0.083*	
C4	0.0928 (3)	0.7347 (3)	0.05022 (17)	0.0675 (8)	
H4A	0.10053	0.628507	0.056467	0.101*	
H4B	0.122638	0.767543	0.007913	0.101*	
H4C	0.014696	0.761126	0.032261	0.101*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02977 (15)	0.03496 (17)	0.03503 (17)	0	0.01136 (12)	0
Cl1	0.0366 (2)	0.0455 (3)	0.0358 (2)	0.00580 (19)	0.00738 (18)	0.00353 (19)
Cl2	0.0601 (3)	0.0429 (3)	0.0653 (4)	0.0098 (2)	0.0367 (3)	-0.0012 (2)
N1	0.0331 (8)	0.0453 (10)	0.0401 (9)	0.0091 (7)	0.0129 (7)	-0.0022 (7)
C1	0.042 (3)	0.0422 (18)	0.040 (2)	-0.0022 (15)	0.0234 (18)	0.0028 (14)
C2	0.0476 (16)	0.0459 (17)	0.0437 (16)	0.0085 (14)	0.0186 (13)	0.0044 (13)
Cl3	0.0477 (5)	0.0645 (6)	0.0649 (6)	-0.0009 (4)	0.0280 (4)	0.0002 (4)
C1A	0.042 (7)	0.083 (8)	0.043 (6)	-0.022 (5)	0.027 (4)	-0.003 (5)
C2A	0.055 (5)	0.052 (4)	0.042 (4)	0.001 (4)	0.023 (3)	0.008 (3)
Cl3A	0.110 (2)	0.0557 (13)	0.0823 (17)	-0.0148 (13)	0.0536 (16)	0.0132 (12)
C3	0.0694 (16)	0.0485 (13)	0.0532 (13)	-0.0096 (11)	0.0288 (12)	0.0008 (10)
C4	0.0780 (19)	0.0693 (18)	0.0481 (13)	0.0019 (15)	0.0139 (13)	-0.0172 (13)

Geometric parameters (Å, °)

Zn1—C12	2.2553 (5)	C2—H2B	0.97
Zn1—C12 ⁱ	2.2554 (5)	C1A—C2A	1.481 (12)
Zn1—C11 ⁱ	2.2883 (5)	C1A—H1C	0.97
Zn1—C11	2.2883 (5)	C1A—H1D	0.97
N1—C1A	1.476 (9)	C2A—C13A	1.765 (8)
N1—C3	1.480 (3)	C2A—H2C	0.97
N1—C4	1.485 (3)	C2A—H2D	0.97
N1—C1	1.515 (5)	C3—H3A	0.96
N1—H1	0.87 (3)	C3—H3B	0.96
C1—C2	1.535 (5)	C3—H3C	0.96
C1—H1A	0.97	C4—H4A	0.96
C1—H1B	0.97	C4—H4B	0.96
C2—C13	1.779 (3)	C4—H4C	0.96
C2—H2A	0.97		
C12—Zn1—C12 ⁱ	118.93 (3)	H2A—C2—H2B	108.1
C12—Zn1—C11 ⁱ	104.94 (2)	N1—C1A—C2A	105.4 (7)
C12 ⁱ —Zn1—C11 ⁱ	108.36 (2)	N1—C1A—H1C	110.7
C12—Zn1—C11	108.36 (2)	C2A—C1A—H1C	110.7
C12 ⁱ —Zn1—C11	104.94 (2)	N1—C1A—H1D	110.7
C11 ⁱ —Zn1—C11	111.38 (3)	C2A—C1A—H1D	110.7
C1A—N1—C3	119.8 (5)	H1C—C1A—H1D	108.8
C1A—N1—C4	111.1 (8)	C1A—C2A—C13A	103.8 (6)
C3—N1—C4	110.5 (2)	C1A—C2A—H2C	111
C3—N1—C1	105.3 (2)	C13A—C2A—H2C	111
C4—N1—C1	114.6 (3)	C1A—C2A—H2D	111
C1A—N1—H1	103.7 (19)	C13A—C2A—H2D	111
C3—N1—H1	106.0 (18)	H2C—C2A—H2D	109
C4—N1—H1	104.1 (18)	N1—C3—H3A	109.5
C1—N1—H1	116.1 (18)	N1—C3—H3B	109.5
N1—C1—C2	116.3 (4)	H3A—C3—H3B	109.5
N1—C1—H1A	108.2	N1—C3—H3C	109.5
C2—C1—H1A	108.2	H3A—C3—H3C	109.5
N1—C1—H1B	108.2	H3B—C3—H3C	109.5
C2—C1—H1B	108.2	N1—C4—H4A	109.5
H1A—C1—H1B	107.4	N1—C4—H4B	109.5
C1—C2—C13	110.7 (3)	H4A—C4—H4B	109.5
C1—C2—H2A	109.5	N1—C4—H4C	109.5
C13—C2—H2A	109.5	H4A—C4—H4C	109.5
C1—C2—H2B	109.5	H4B—C4—H4C	109.5
C13—C2—H2B	109.5		
C3—N1—C1—C2	178.5 (4)	C3—N1—C1A—C2A	157.7 (7)

C4—N1—C1—C2	−59.9 (6)	C4—N1—C1A—C2A	−71.4 (12)
N1—C1—C2—Cl3	−61.3 (6)	N1—C1A—C2A—Cl3A	179.3 (9)

Symmetry code: (i) $-x+1, y, -z+1/2$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N1—H1 \cdots Cl1 ⁱ	0.87 (3)	2.51 (3)	3.3124 (18)	156 (2)
N1—H1 \cdots Cl2	0.87 (3)	3.03 (3)	3.5620 (19)	121 (2)

Symmetry code: (i) $-x+1, y, -z+1/2$.