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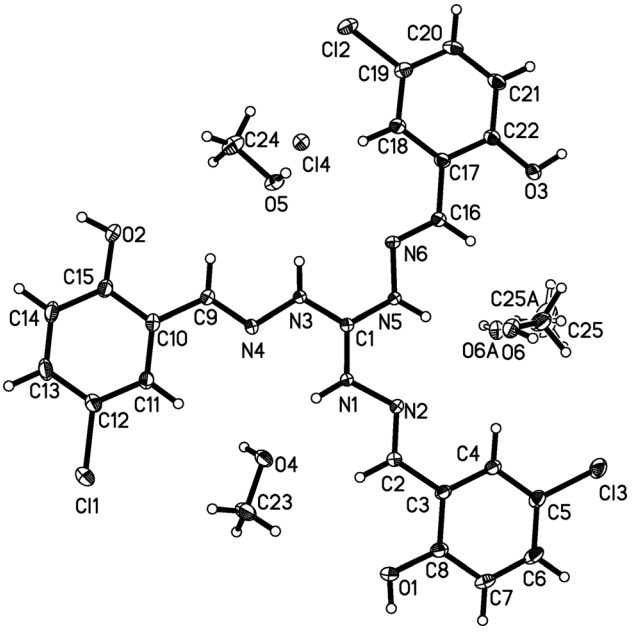
The crystal structure of *N′*,*N″*,2-tris((*E*)-5-chloro-2-hydroxybenzylidene)hydrazine-1-carbohydrazonhydrazide hydrochloride – methanol (1/3), $C_{25}H_{30}Cl_4N_6O_6$



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Abstract

$C_{25}H_{30}Cl_4N_6O_6$, triclinic, $P\bar{1}$ (no. 2), a = 9.2652(2) Å, b = 11.7642(3) Å, c = 14.6692(4) Å, α = 106.929(2)°, β = 99.753(2)°, γ = 98.675(2)°, V = 1473.15(7) Å^3, Z = 2, $R_{gt}(F)$ = 0.0292, $wR_{ref}(F^2)$ = 0.0839, T = 170 K.

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Table 1: Data collection and handling.

Crystal:	Pink block
Size:	0.31 × 0.15 × 0.12 mm
Wavelength:	Cu *K*α radiation (1.54184 Å)
μ:	4.09 mm^{-1}
Diffractometer, scan mode:	XTALAB Synergy R, ω
θ_{max}, completeness:	77.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	18,336, 5986, 0.020
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 5692
$N(param)_{refined}$:	400
Programs:	CrysAlis^{PRO} [1], Olex2 [2], SHELX [3, 4]

Source of material

5-Chlorosalicylaldehyde (4.69 g, 0.01 mol) was placed in 15 mL ethanol at room temperature, then added into triaminoguanidine hydrochloride (1.40 g, 0.01 mol) solution containing 10 mL water and 8 mL ethanol. The mixture was heated and stirred at 65 °C for 3 h, and finally cooled to room temperature, Then remove the sediment was removed and the obtained filtrate stands for three days to precipitate light pink block crystals.

Experimental details

The crystal data collection was done on a XTALAB Synergy R, HYPIX diffractometer [1]. Using Olex2 [2], the structure was solved with the SHELXT [3] structure solution program and refined with the SHELXL [4] refinement package. All

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Cl1	0.66164 (5)	0.18556 (3)	0.12521 (3)	0.04561 (11)
Cl2	−0.09921 (4)	0.99436 (3)	0.20952 (3)	0.04146 (10)
Cl3	0.77613 (4)	0.96687 (3)	0.94730 (2)	0.04106 (10)
O1	0.88354 (11)	0.52448 (9)	0.67899 (7)	0.0360 (2)
H1	0.951147	0.498117	0.707228	0.054*
O2	0.26637 (12)	0.47623 (9)	−0.01314 (7)	0.0367 (2)
H2	0.237084	0.449433	−0.074334	0.055*
O3	0.23621 (11)	1.17478 (8)	0.61925 (7)	0.0321 (2)
H3	0.202833	1.231584	0.652679	0.048*
N1	0.54046 (12)	0.65597 (9)	0.46849 (7)	0.0250 (2)
H1A	0.561322	0.588724	0.433015	0.030*
N2	0.59646 (11)	0.70307 (9)	0.56865 (7)	0.0242 (2)
N3	0.40530 (11)	0.68274 (9)	0.33138 (7)	0.0238 (2)
H3A	0.349003	0.722790	0.303578	0.029*
N4	0.44751 (11)	0.58122 (9)	0.27617 (7)	0.0242 (2)
N5	0.41405 (12)	0.81334 (9)	0.48564 (7)	0.0249 (2)
H5	0.447451	0.838692	0.549540	0.030*
N6	0.31906 (11)	0.87128 (9)	0.44088 (7)	0.0240 (2)
C1	0.45322 (13)	0.71731 (10)	0.42812 (8)	0.0217 (2)
C2	0.68857 (14)	0.64710 (11)	0.60325 (9)	0.0262 (2)
H2A	0.709754	0.576569	0.560963	0.031*
C3	0.76136 (13)	0.69054 (11)	0.70701 (9)	0.0252 (2)
C4	0.73543 (14)	0.79538 (11)	0.77063 (9)	0.0272 (3)
H4	0.667221	0.838575	0.747037	0.033*
C5	0.80885 (15)	0.83617 (12)	0.86769 (9)	0.0302 (3)
C6	0.90966 (16)	0.77488 (13)	0.90348 (10)	0.0363 (3)
H6	0.960310	0.804427	0.970474	0.044*
C7	0.93604 (15)	0.67087 (13)	0.84138 (10)	0.0346 (3)
H7	1.004783	0.628599	0.865735	0.041*
C8	0.86217 (14)	0.62765 (12)	0.74305 (10)	0.0281 (3)
C9	0.39335 (14)	0.54939 (11)	0.18402 (9)	0.0257 (2)
H9	0.332087	0.596329	0.159111	0.031*
C10	0.42423 (14)	0.44201 (11)	0.11654 (9)	0.0260 (2)
C11	0.51707 (14)	0.37243 (11)	0.14974 (9)	0.0279 (3)
H11	0.562633	0.394950	0.217312	0.033*
C12	0.54232 (16)	0.27096 (12)	0.08405 (10)	0.0326 (3)
C13	0.47444 (18)	0.23478 (13)	−0.01452 (10)	0.0381 (3)
H13	0.491472	0.163695	−0.058655	0.046*
C14	0.38191 (17)	0.30248 (13)	−0.04833 (10)	0.0354 (3)
H14	0.335284	0.277986	−0.115869	0.042*
C15	0.35678 (15)	0.40682 (12)	0.01657 (9)	0.0289 (3)
C16	0.28616 (14)	0.96367 (11)	0.49841 (9)	0.0257 (2)
H16	0.329460	0.989287	0.566521	0.031*
C17	0.18291 (13)	1.03014 (11)	0.46062 (9)	0.0248 (2)
C18	0.10420 (14)	0.98776 (11)	0.36259 (9)	0.0277 (3)
H18	0.121806	0.917093	0.318264	0.033*
C19	0.00126 (14)	1.04895 (12)	0.33078 (10)	0.0295 (3)
C20	−0.02548 (15)	1.15270 (12)	0.39405 (11)	0.0327 (3)
H20	−0.096956	1.193809	0.371023	0.039*
C21	0.05215 (15)	1.19622 (12)	0.49080 (10)	0.0312 (3)
H21	0.034503	1.267657	0.534124	0.037*
C22	0.15622 (14)	1.13545 (11)	0.52481 (9)	0.0259 (2)
Cl4	−0.13211 (3)	0.60410 (3)	0.24272 (2)	0.03116 (9)
O4	0.72925 (13)	0.50240 (9)	0.39093 (8)	0.0394 (2)
H4A	0.764360	0.524568	0.348195	0.059*
C23	0.7849 (2)	0.40109 (15)	0.40234 (13)	0.0447 (4)
H23A	0.728822	0.327590	0.349158	0.067*
H23B	0.773275	0.392190	0.465238	0.067*
H23C	0.891222	0.413050	0.400547	0.067*
O5	0.16415 (11)	0.72976 (10)	0.20877 (7)	0.0384 (2)
H5A	0.087527	0.701953	0.225399	0.058*
C24	0.1235 (2)	0.73236 (18)	0.11198 (12)	0.0506 (4)
H24A	0.051216	0.657412	0.071530	0.076*
H24B	0.212972	0.738943	0.084972	0.076*
H24C	0.078095	0.802526	0.112483	0.076*
O6[a]	0.44043 (16)	0.91932 (12)	0.69584 (9)	0.0378 (4)
H6A[a]	0.401499	0.891210	0.734590	0.057*
C25[a]	0.5144 (6)	1.0382 (5)	0.7439 (4)	0.0496 (14)
H25A[a]	0.581853	1.063958	0.705485	0.074*
H25B[a]	0.572862	1.044965	0.808221	0.074*
H25C[a]	0.441286	1.090370	0.752128	0.074*
O6A[b]	0.5538 (5)	0.9895 (4)	0.6780 (3)	0.0375 (14)
H6AA[b]	0.610989	1.031171	0.655511	0.056*
C25A[b]	0.523 (3)	1.057 (2)	0.7509 (19)	0.072 (7)
H25D[b]	0.485257	1.123396	0.734595	0.108*
H25E[b]	0.613737	1.090115	0.803708	0.108*
H25F[b]	0.446680	1.010026	0.772157	0.108*

[a]Occupancy: 0.776 (3), [b]Occupancy: 0.224 (3).

H-atoms were placed geometrically and refined using a riding model with common isotropic displacement factors U_{iso}(H) = 1.2 or 1.5 U_{eq} (parent C-atom).

Comment

As a good building block, triaminoguanidinium chloride and its derivatives are widely used in coordination chemistry [5, 6]. In addition, because triaminoguanidinium chloride contains rich N atoms and has good biological activity, it is also used in the research field of energetic materials [7] and biomedicine [8]. As far as we know, there are four reported structures of salts containing a triaminoguanidine-based Schiff base cation [10–13]. We synthesized the title compound on the basis of previous studies.

The asymmetric units of the title compound include one $[C_{22}H_{18}Cl_3N_6O_3]^+$ cation, one Cl^- anion and three solvent methanol molecules (see the figure). They are connected by O–H···Cl and N–H···O weak intermolecular hydrogen bonds, which makes the structure of the whole compound more stable. In the title compound, the bond lengths of N_2=C_2, N_4=C_9 and N_6=C_{16} are 1.279 (2), 1.279(2) and 1.280(2) Å respectively. They are basically consistent

with the reported C=N (1.279 Å) [9] double bond lengths of similar structures. Other bond lengths and bond angles are also within the normal range.

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References

1. Oxford Diffraction Ltd. CrysAlis^{PRO} *(Version 1.171.41.121a)*; Rigaku Oxford Diffraction: England, 2021.
2. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, *42*, 339–341.
3. Sheldrick G. M. *SHELXTL* – Integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.
4. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
5. Plaul D., Bohme M., Ostrovsky S., Tomkowicz Z., Gorls H., Haase W., Plass W. Modeling spin interactions in a triangular cobalt(II) complex with triaminoguanidine ligand framework: synthesis, structure, and magnetic properties. *Inorg. Chem.* 2018, *57*, 106–119.
6. Zharkouskaya A., Gorls H., Vaughan G., Plass W. A new three-dimensional Cu(II) coordination polymer with triaminoguanidin building blocks. *Inorg. Chem. Commun.* 2005, *8*, 1145–1148.
7. Yan Q. L., Cohen A., Chinnam A. K., Petrutik N., Shlomovich A., Burstein L., Gozin M. A layered 2D triaminoguanidine-glyoxal polymer and its transition metal complexes as novel insensitive energetic nanomaterials. *J. Mater. Chem. A* 2016, *4*, 18401–18408.
8. Muthusamy S., Zhu D. W., Rajalakshmi K., Zhu W. H., Wang S. J., Lee K. B., Zhao L. Successive detection of zinc ion and citrate using a Schiff base chemosensor for enhanced prostate cancer diagnosis in biosystems. *ACS Appl. Bio Mater.* 2011, *4*, 1932–1941.
9. Müller I. M., Möller D. A New ligand for the formation of triangular building blocks in supramolecular chemistry. *Eur. J. Inorg. Chem.* 2005, *2*, 257–263.
10. Müller I. M., Möller D., Schalley C. A. Rational design of tightly closed coordination tetrahedra that are stable in the solid state, in solution, and in the gas phase. *Angew. Chem. Int. Ed.* 2005, *44*, 480–484.
11. Singh H., Devi M., Jena N., Iqbal M. M., Nailwal Y., De Sarkar A., Pal S. K. Proton-triggered fluorescence switching in self-exfoliated ionic covalent organic nanosheets for applications in selective detection of anions. *ACS Appl. Mater. Interfaces* 2020, *12*, 13248–13255.
12. Mitra S., Kandambeth S., Biswal B. P., Khayum M. A., Choudhury C. K., Mehta M., Kaur G., Banerjee S., Prabhune A., Verma S., Roy S., Kharu U. K., Banerjee R. Self-exfoliated guanidinium-based ionic covalent organic nanosheets (iCONs). *J. Am. Chem. Soc.* 2016, *138*, 2823–2828.
13. Jia A. Q., Zhou W. Y., Wu S. M., Shi H. T., Zhang Q. F. Cis-dioxo-molybdenum(VI) complexes with diaminoguanidinium and triaminoguanidinium Schiff bases and their catalytic application for epoxidation of cyclohexene. *ChemistrySelect* 2020, *5*, 11085–11095.