Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

5,7-Dimethyl-1,2,4-triazolo[1,5-*a*]pyrimidinium tetrachlorocobaltate(II) monohydrate

Carmen R. Maldonado, Miguel Quirós,* Juan M. Salas and M. Purificación Sánchez

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain

Correspondence e-mail: mquiros@ugr.es

Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.003 Å
R factor = 0.031
wR factor = 0.080
Data-to-parameter ratio = 18.5

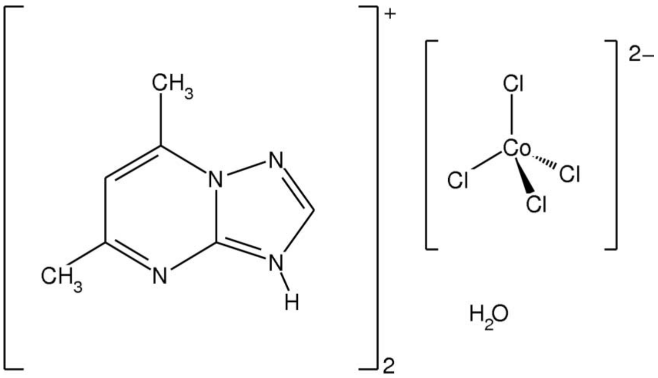
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 5 July 2005
Accepted 1 August 2005
Online 6 August 2005

The asymmetric unit of the title compound, $(C_7H_8N_4)_2[CoCl_4]\cdot H_2O$, contains one $[CoCl_4]^{2-}$ anion, two 5,7-dimethyl-1,2,4-triazolo[1,5-*a*]pyrimidinium cations monoprotonated at the N atom at position 3 and one uncoordinated water molecule. Hydrogen bonds define infinite chains along the *a* axis, which link together all residues.

Comment

1,2,4-Triazolo-[1.5-*a*]pyrimidine derivatives are well known N-donor heterocyclic ligands and have been extensively studied by us, as well as by other research groups (Salas *et al.*, 1999). Some of these ligands are known to be unstable in an acidic medium, where they decompose giving 3-amino-1,2,4-triazole; this decomposition seems to be promoted by the presence of transition metal ions (Sánchez *et al.*, 2004). Other 1,2,4-triazolo[1.5-*a*]pyrimidine derivatives, however, are fairly stable, even at very low pH. The 5,7-dimethyl derivative (dmtp), for example, is easily stabilized as a cationic species protonated at N3, the charge of this cation being balanced by anionic metal complexes such as $[CdBr_4]^{2-}$ (Salas *et al.*, 1996), $[SnCl_6]^{2-}$ (Salas *et al.*, 1998) or $[PtCl_6]^{2-}$ (Szlyk *et al.*, 2002). The structure, which is reported in this paper, adds one more salt to this series, where the charge of the cation is balanced by the tetrachlorocobaltate(II) anion.



(I)

The crystal structure of the title compound, (I), is made up of discrete $[CoCl_4]^{2-}$ anions, 5,7-dimethyl-1,2,4-triazolo-[1,5-*a*]pyrimidinium ($Hdmtp^+$) cations and uncoordinated water molecules. All residues occupy general positions, the asymmetric unit containing one anion, two crystallographically independent but chemically identical cations and one water molecule. A view of the asymmetric unit is shown in Fig. 1.

The anion displays a considerable distortion from the ideal T_d symmetry (see distances and angles in Table 1), a normal behaviour for $[CoCl_4]^{2-}$, which seems to be a very flexible species, and according to the statistical analysis by Haddad *et al.* (2003) exhibits substantial variability in Cl—Co—Cl bond angles. The average Co—Cl bond distance in the title compound, 2.2711 Å, is quite similar to the overall average value of 2.2725 Å, as reported by Haddad *et al.* (2003).

The site of protonation of the organic residue at N3 is clear from the ΔF maps and from the strong hydrogen bonds formed with the water molecule or one of the Cl atoms of the anion as acceptors (see Table 2). The main difference in the geometry of protonated dmtp compared with that of the neutral species is the widening of the endocyclic bond angle at N3, which is 106.8 (2) and 106.4 (2)° in the two independent cations of the title compound, whereas the corresponding angle in free dmtp is 102.2 (3)° (Salas *et al.*, 1994). Such widening of the bond angle at the protonated N atom is quite common and was also observed in the above-mentioned ionic structures containing $dmtpH^+$.

It is interesting to mention the existence of a rather short contact between the Cl atoms of the anion and the bridgehead N atoms of the cations, N8*A* and N8*B*. These contacts [Cl1···N8*B* = 3.287 (2) Å and Cl2···N8*A* = 3.235 (1) Å] are most probably of electrostatic nature, the Cl1···N8*B* and Cl2···N8*A* vectors being approximately orthogonal to the plane of the heterocycle; the normal to this plane forms angles of 2.89 (3) and 4.86 (2)° with Cl1···N8*B* and Cl12···N8*A*, respectively. In the structure of the title compound, there are also several hydrogen bonds, involving the H atoms at N3*A* and N3*B* (see above) as well the H atoms of the water molecule (Table 2). These hydrogen bonds link together all residues, defining infinite chains running along the *a* axis.

Experimental

An aqueous solution of cobalt(II) chloride hexahydrate (1 mmol, 10 ml) and a solution of dmtp in 1:1 HCl (2 mmol, 20 ml) were mixed. The mixture was allowed to evaporate at room temperature and, after 24 h, blue prismatic crystals of the title compound were obtained. Analysis found: C 32.48, H 4.23, N 21.75%; calculated: C 32.52, H 3.90, N 21.67%.

Crystal data

$2C_7H_9N_4^+ \cdot Cl_4Co^{2-} \cdot H_2O$
$M_r = 517.11$
Triclinic, $P\bar{1}$
$a = 7.6369\ (4)$ Å
$b = 8.5190\ (4)$ Å
$c = 18.2777\ (9)$ Å
$\alpha = 84.952\ (1)^\circ$
$\beta = 84.505\ (1)^\circ$
$\gamma = 65.275\ (1)^\circ$
$V = 1073.64\ (9)$ Å^3
$Z = 2$
$D_x = 1.600$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5772 reflections
$\theta = 2.2$–27.2°
$\mu = 1.32$ mm^{-1}
$T = 298\ (2)$ K
Prism, blue
0.46 × 0.29 × 0.23 mm

Data collection

Bruker SMART APEX CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min} = 0.668$, $T_{max} = 0.751$
12624 measured reflections
4866 independent reflections
4217 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 28.3^\circ$
$h = -9 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -24 \rightarrow 23$

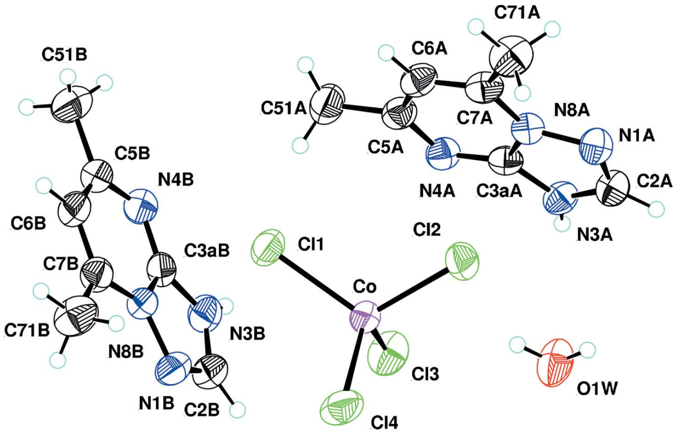


Figure 1
The asymmetric unit of the title compound, with the non-H atoms represented by 50% probability displacement ellipsoids; H atoms are shown as circles of arbitrary radius.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.080$
$S = 1.04$
4866 reflections
263 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 0.25P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co—Cl1	2.2898 (5)	Co—Cl3	2.2583 (6)
Co—Cl2	2.2697 (5)	Co—Cl4	2.2666 (6)
Cl3—Co—Cl4	112.31 (3)	Cl3—Co—Cl1	112.49 (2)
Cl3—Co—Cl2	107.13 (2)	Cl4—Co—Cl1	104.59 (2)
Cl4—Co—Cl2	108.47 (3)	Cl2—Co—Cl1	111.86 (2)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3*A*—H3*A*···O1*W*^{i}	0.86	1.83	2.681 (2)	171
N3*B*—H3*B*···Cl1	0.86	2.31	3.1325 (18)	160
O1*W*—H11*W*···N1*A*^{ii}	0.84 (1)	2.19 (1)	3.026 (2)	169 (2)
O1*W*—H12*W*···Cl2	0.84 (1)	2.59 (2)	3.3122 (15)	144 (2)

Symmetry codes: (i) $-x, -y+1, -z$; (ii) $-x+1, -y+1, -z$.

H atoms of the organic cations were idealized (C—H 0.93 and 0.96 Å, and N—H = 0.86 Å). Those of the water molecule were located in a ΔF map and refined with restrained O—H [0.86 (1) Å] and H···H distances [1.36 (1) Å]. Isotropic displacement parameters of all H atoms were set to be 1.2 times U_{eq} of their parent atoms.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine

m1722 Maldonado *et al.* • $2C_7H_9N_4^+ \cdot Cl_4Co^{2-} \cdot H_2O$ *Acta Cryst.* (2005). E**61**, m1721–m1723

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Xtal_GX* (Hall & du Boulay, 1997); software used to prepare material for publication: *SHELXL97*.

We acknowledge financial support from the Spanish Ministerio de Ciencia *y* Tecnología (project BQU 2001-2955-CO2) and from the Junta de Andalucía (research group FQM 0195).

References

Bruker (1999). *SADABS*, *SMART* and *SAINT*. Bruker AXS Inc., Madison, Winsconsin, USA.

Haddad, S., Vij, A. & Willett, R. D. (2003). *J. Chem. Crystallogr.* **33**, 245–251.

Hall, S. R. & du Boulay, D. (1997). *Xtal_GX*. University of Western Australia, Perth, Australia.

Salas, J. M., Rahmani, A., Romero, M. A., Quirós, M. & Tiekink, E. R. T. (1994). *J. Chem. Crystallogr.* **24**, 669–673.

Salas, J. M., Rahmani, A., Romero, M. A., Rae, A. D., Willis, A. C. & Tiekink, E. R. T. (1998). *Z. Kristallogr.* **213**, 302–304.

Salas, J. M., Romero, M. A., Rahmani, A., Faure, R., Álvarez de Cienfuegos, G. & Tiekink, E. R. T. (1996). *J. Inorg. Biochem.* **64**, 259–271.

Salas, J. M., Romero, M. A., Sánchez, M. P. & Quirós, M. (1999). *Coord. Chem. Rev.* **195**, 1119–1142.

Sánchez, C., Salas, J. M., Quirós, M. & Sánchez, M. P. (2004). *Acta Cryst.* E**60**, m370–m372.

Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.

Szlyk, E., Pazderski, L., Lakomska, I., Surdykowski, A., Glowiak, T., Sitkowski, J. & Kozerski, L. (2002). *Polyhedron*, **21**, 343–348.

Acta Cryst. (2005). E**61**, m1721–m1723 Maldonado *et al.* • $2C_7H_9N_4^+ \cdot Cl_4Co^{2-} \cdot H_2O$ **m1723**