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# Bis[tetraamminezinc(II)] tetrapicrate trihydrate

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**Key indicators**

Single-crystal X-ray study
*T* = 298 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
*R* factor = 0.039
*wR* factor = 0.097
Data-to-parameter ratio = 10.5

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



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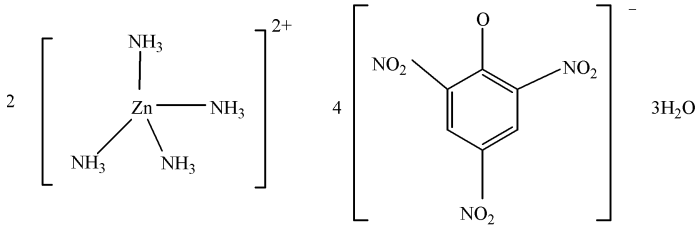
In the title compound, $[Zn(NH_3)_4](C_6H_2N_3O_7)_4\cdot 3H_2O$, the $Zn^{II}$ atom is coordinated by four ammine N atoms in a slightly distorted tetrahedron. The phenolate and nitro O atoms of the picrate ions act as acceptors in N—H···O and O—H···O hydrogen bonds, giving a three-dimensional network.

## Comment

For many purposes, including catalysis, it is desirable to utilize transition metal complexes that contain anions which coordinate weakly or not at all (Batsanov *et al.*, 2001). We report here the structure of the title compound, (I).




(I)

In (I), there are two $[Zn(NH_3)_4]^{2+}$ cations, four picrate anions and three water molecules of crystallization in the asymmetric unit (Fig. 1). The mean Zn—N bond length is 2.008 (14) Å, which is comparable to the value of 2.052 (8) Å observed in tetraamminezinc octahydrooctaborate (Guggenberger, 1969) and that of 2.038 (12) Å in tetraamminezinc C60-fulleride ammonia (Brumm & Jansen, 2001). The N—Zn—N bond angles around Zn1 and Zn2 range from 104.57 (10) to 112.27 (12)°, indicating a slightly distorted tetrahedral geometry. The C—O bond length of the phenolate indicates a partial double bond, implying that the negative charge located on the phenolate O atom is delocalized over the whole C—O bond. In the crystal structure, the phenolate and nitro O atoms of the picrate ions act as acceptors in O—H···O and N—H···O hydrogen bonds (Table 2), giving a three-dimensional network.

## Experimental

All reagents and solvents were used as obtained without further purification. ZnO (0.3 mmol, 24 mg) and picric acid (0.6 mmol, 138 mg) were dissolved in 30% aqueous ammonia (15 ml). The mixture was stirred for 1 h to obtain a clear yellow solution. After keeping the solution in air for two weeks with ammonia gas escaping, crystals of (I) were formed. The product was isolated, washed three times with water, and dried in a vacuum desiccator using $P_4O_{10}$ (yield 52%). Elemental analysis calculated: C 23.37, H 3.11, O 40.21, N 22.71, Zn 10.60%; found: C 23.21, H 3.63, O 40.31, N 22.67, Zn 10.12%.

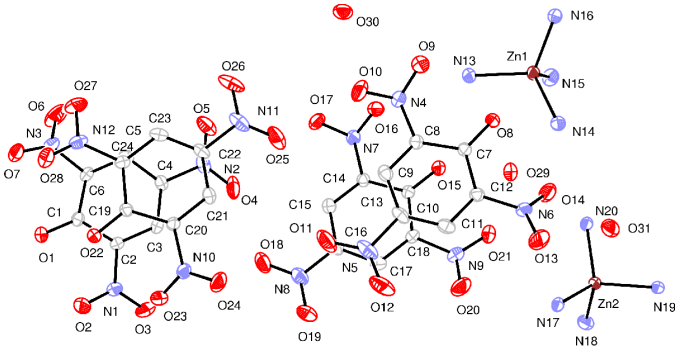



**Figure 1**
The asymmetric unit of the title compound, showing 30% probability displacement ellipsoids. One of two possible orientations of the disordered nitro groups and H atoms have been omitted for clarity.

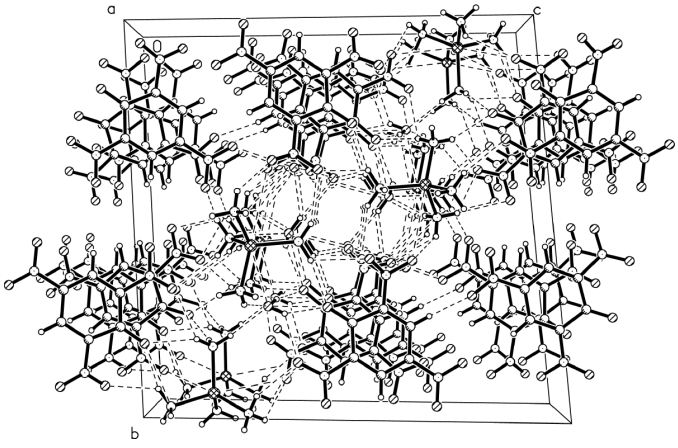



**Figure 2**
The crystal packing of (I), viewed along the *a* axis. Dashed lines indicate hydrogen bonds.

*Crystal data*

$[Zn(NH_3)_4](C_6H_2N_3O_7)_4\cdot 3H_2O$
$M_r$ = 1233.48
Triclinic, $P\overline{1}$
$a$ = 7.056 (4) Å
$b$ = 18.202 (9) Å
$c$ = 18.715 (9) Å
$\alpha$ = 85.002 (7)°
$\beta$ = 83.941 (7)°
$\gamma$ = 80.575 (6)°
$V$ = 2352 (2) Å$^3$
$Z$ = 2
$D_x$ = 1.742 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 800 reflections
$\theta$ = 2.3–25.0°
$\mu$ = 1.14 mm$^{-1}$
$T$ = 298 (2) K
Block, yellow
0.56 × 0.48 × 0.41 mm

*Data collection*

Bruker SMART CCD area-detector diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.567, $T_{max}$ = 0.652
12336 measured reflections
8171 independent reflections
5571 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.021
$\theta_{max}$ = 25.0°
$h = -8 \rightarrow 8$
$k = -19 \rightarrow 21$
$l = -22 \rightarrow 17$

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.097
$S$ = 0.92
8171 reflections
775 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0545P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.46 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.45 e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Zn1—N16 | 1.995 (3) | Zn2—N19 | 2.019 (3) |
| Zn1—N15 | 1.998 (3) | Zn2—N18 | 2.035 (3) |
| Zn1—N14 | 2.001 (3) | C1—O1 | 1.241 (3) |
| Zn1—N13 | 2.002 (3) | C7—O8 | 1.254 (3) |
| Zn2—N20 | 2.000 (3) | C13—O15 | 1.231 (3) |
| Zn2—N17 | 2.007 (3) | | |
| N16—Zn1—N15 | 107.82 (13) | N20—Zn2—N17 | 116.70 (10) |
| N16—Zn1—N14 | 112.27 (12) | N20—Zn2—N19 | 104.57 (10) |
| N15—Zn1—N14 | 109.12 (12) | N17—Zn2—N19 | 110.77 (12) |
| N16—Zn1—N13 | 109.94 (11) | N20—Zn2—N18 | 111.62 (12) |
| N15—Zn1—N13 | 108.79 (13) | N17—Zn2—N18 | 106.30 (12) |
| N14—Zn1—N13 | 108.83 (11) | N19—Zn2—N18 | 106.50 (12) |

**Table 2**
Hydrogen-bonding geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O29—H29$A$···O15 | 0.834 (10) | 2.059 (19) | 2.814 (4) | 150 (3) |
| O29—H29$A$···O21′ | 0.834 (10) | 2.31 (3) | 2.946 (14) | 133 (3) |
| O29—H29$A$···O21 | 0.834 (10) | 2.38 (2) | 3.039 (12) | 137 (3) |
| O30—H30$A$···O10′ | 0.822 (10) | 2.26 (2) | 2.944 (9) | 141 (3) |
| O30—H30$A$···O9′ | 0.822 (10) | 2.403 (14) | 3.220 (9) | 173 (3) |
| O30—H30$A$···O9 | 0.822 (10) | 2.628 (18) | 3.403 (9) | 158 (3) |
| O31—H31$A$···O1$^{i}$ | 0.844 (10) | 2.035 (16) | 2.829 (3) | 156 (3) |
| O31—H31$A$···O2$^{i}$ | 0.844 (10) | 2.58 (3) | 3.095 (4) | 120 (3) |
| O29—H29$B$···O8$^{ii}$ | 0.836 (10) | 2.136 (15) | 2.932 (4) | 159 (3) |
| O30—H30$B$···O8$^{iii}$ | 0.832 (10) | 1.997 (11) | 2.813 (4) | 167 (3) |
| O30—H30$B$···O9$^{iii}$ | 0.832 (10) | 2.39 (3) | 2.861 (8) | 117 (2) |
| O30—H30$B$···O9′$^{iii}$ | 0.832 (10) | 2.63 (3) | 3.172 (11) | 125 (2) |
| O31—H31$B$···O14 | 0.835 (10) | 2.160 (15) | 2.967 (4) | 162 (3) |
| N13—H13$A$···O16′$^{iv}$ | 0.89 | 2.58 | 3.137 (7) | 122 |
| N13—H13$B$···O15 | 0.89 | 2.26 | 3.065 (4) | 151 |
| N13—H13$B$···O16 | 0.89 | 2.66 | 3.106 (6) | 112 |
| N13—H13$C$···O30$^{iv}$ | 0.89 | 2.41 | 3.233 (5) | 153 |
| N14—H14$A$···O29 | 0.89 | 2.31 | 3.043 (4) | 140 |
| N14—H14$B$···O8 | 0.89 | 2.21 | 3.067 (4) | 160 |
| N14—H14$B$···O14 | 0.89 | 2.43 | 3.032 (4) | 126 |
| N14—H14$C$···O7$^{i}$ | 0.89 | 2.39 | 3.116 (4) | 139 |
| N14—H14$C$···O1$^{i}$ | 0.89 | 2.41 | 3.207 (4) | 148 |
| N15—H15$A$···O26$^{iv}$ | 0.89 | 2.35 | 2.976 (4) | 128 |
| N15—H15$A$···O5$^{iv}$ | 0.89 | 2.64 | 3.459 (4) | 153 |
| N15—H15$B$···O30$^{iv}$ | 0.89 | 2.19 | 3.052 (4) | 163 |
| N15—H15$C$···O28′$^{v}$ | 0.89 | 2.33 | 3.177 (13) | 158 |
| N15—H15$C$···O28$^{v}$ | 0.89 | 2.49 | 3.260 (12) | 145 |
| N16—H16$A$···O6$^{i}$ | 0.89 | 2.49 | 3.370 (5) | 170 |
| N16—H16$A$···O7$^{i}$ | 0.89 | 2.55 | 3.162 (4) | 126 |
| N16—H16$A$···O26$^{iii}$ | 0.89 | 2.58 | 3.049 (4) | 114 |
| N16—H16$B$···O30$^{iii}$ | 0.89 | 2.31 | 3.154 (5) | 158 |
| N16—H16$C$···O17′$^{iv}$ | 0.89 | 2.26 | 3.045 (8) | 147 |
| N16—H16$C$···O10$^{iii}$ | 0.89 | 2.49 | 2.935 (7) | 112 |
| N16—H16$C$···O17$^{iv}$ | 0.89 | 2.54 | 3.263 (8) | 139 |
| N17—H17$A$···O21′ | 0.89 | 2.25 | 3.050 (12) | 150 |
| N17—H17$A$···O21 | 0.89 | 2.33 | 3.202 (11) | 165 |
| N17—H17$B$···O24$^{vi}$ | 0.89 | 2.26 | 2.993 (4) | 139 |
| N17—H17$C$···O12$^{vi}$ | 0.89 | 2.48 | 3.281 (4) | 149 |
| N17—H17$C$···O11$^{vi}$ | 0.89 | 2.62 | 3.293 (4) | 133 |
| N18—H18$A$···O19$^{vii}$ | 0.89 | 2.40 | 3.184 (4) | 147 |
| N18—H18$B$···O3$^{vii}$ | 0.89 | 2.60 | 3.328 (5) | 139 |
| N18—H18$C$···O31$^{ii}$ | 0.89 | 2.31 | 3.196 (5) | 180 |
| N19—H19$A$···O22$^{v}$ | 0.89 | 2.06 | 2.903 (3) | 158 |
| N19—H19$A$···O23$^{v}$ | 0.89 | 2.48 | 3.119 (4) | 129 |
| N19—H19$B$···O3$^{vii}$ | 0.89 | 2.25 | 3.072 (4) | 154 |
| N20—H20$A$···O29 | 0.89 | 2.19 | 3.049 (4) | 162 |
| N20—H20$B$···O1$^{v}$ | 0.89 | 2.26 | 3.103 (4) | 158 |
| N20—H20$C$···O22$^{v}$ | 0.89 | 2.28 | 3.062 (3) | 146 |
| N20—H20$C$···O28′$^{v}$ | 0.89 | 2.41 | 3.133 (14) | 139 |

Symmetry codes: (i) $x-1, y, 1+z$; (ii) $1+x, y, z$; (iii) $-x, 1-y, 1-z$; (iv) $1-x, 1-y, 1-z$; (v) $x, y, 1+z$; (vi) $1-x, -y, 1-z$; (vii) $2-x, -y, 1-z$.

There was rotational disorder of the nitro groups, and the site-occupation factors for O9/O10/O16/O17/O21/O28 and O9′/O10′/O16′/O17′/O21′/O28′ are 0.537 (7) and 0.463 (3), respectively. Although the H atoms bonded to N and C atoms were visible in difference maps, they were placed in geometrically calculated positions, and included in the refinement in the riding-model approximation; N—H = 0.89 Å with $U_{iso}(H) = 1.5U_{eq}(N)$, and C—H = 0.93 Å with $U_{iso}(H) = 1.2U_{eq}(C)$. The positional parameters of the water H atoms were refined with restraints on the O—H distance and with $U_{iso}(H) = 0.051$ Å$^2$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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