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Key indicators

Single-crystal X-ray study  
T = 293 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$   
R factor = 0.045  
wR factor = 0.125  
Data-to-parameter ratio = 23.3

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

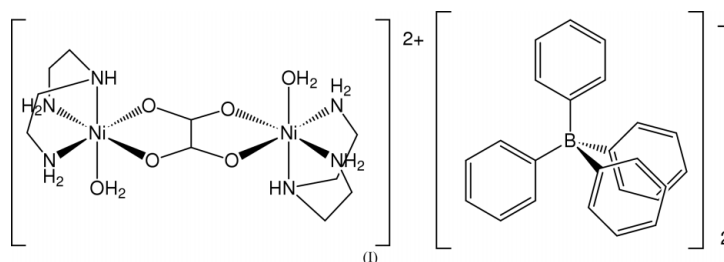
$\mu$ -Oxalato- $\kappa^4\text{O}^1, \text{O}^2: \text{O}^{1'}, \text{O}^{2'}$ -bis[aqua(diethylenetriamine- $\kappa^3\text{N}$ )nickel(II)] bis(tetraphenylborate)

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The title compound,  $[\text{Ni}_2(\text{C}_2\text{O}_4)(\text{C}_4\text{H}_{13}\text{N}_3)_2(\text{H}_2\text{O})_2][\text{B}(\text{C}_6\text{H}_5)_4]_2$ , contains a centrosymmetric dinuclear oxalato-nickel(II) complex cation in which the oxalate ligand bridges the Ni atoms in a bis-bidentate fashion. The distorted octahedral environment of each Ni atom is completed by the three N atoms of the diethylenetriamine ligand in a *fac* arrangement, and by one O atom from a water molecule. Tetraphenylborate acts as the counter-anion. The crystal structure shows alternate cationic and anionic layers packed along the  $[10\bar{1}]$  direction.

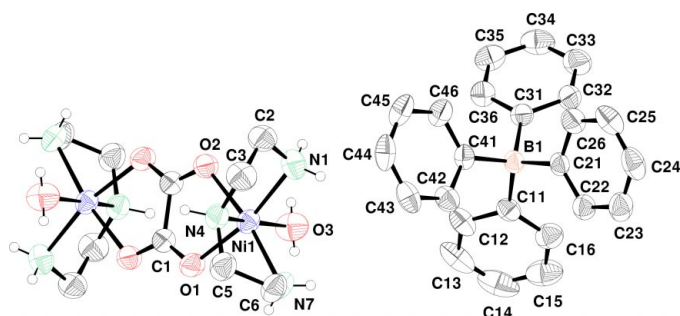
Comment

The remarkable ability of the oxalate bridge to mediate exchange coupling between first-row transition metal ions has attracted a significant interest in the molecular magnetism area during the last 25 years (Cano *et al.*, 1999). One of the most deeply studied systems is the  $\text{Ni}^{\text{II}}$ -oxalate complexes, due to the strong magneto-structural correlations found in these systems (Khan, 1993). In the course of our investigations into molecular magnetic materials based on metal-oxalate dimers, we have synthesized some salts of the  $[\{\text{Ni}(\text{dien})(\text{H}_2\text{O})\}_2(\text{ox})]^{2+}$  complex cation, such as the dichloride (Román *et al.*, 1996), dibromide (Vitoria *et al.*, 2003), dinitrate (Guzmán *et al.*, 2001) and bis(hexafluorophosphate) (Muga *et al.*, 2002), the diperchlorate monohydrate being also known (Travnicek *et al.*, 1997). These salts can be used as precursors in the synthesis of pseudohalide (Muga *et al.*, 2000) or cyanometalate derivatives (Muga *et al.*, 1997) owing to the extreme lability of their water molecules.

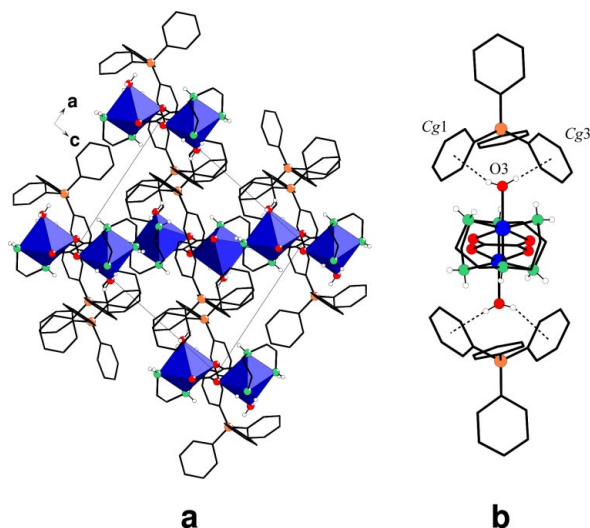


We report here the synthesis and crystal structure of a new salt of the above-mentioned complex cation,  $[\{\text{Ni}(\text{dien})(\text{H}_2\text{O})\}_2(\text{ox})][\text{B}(\text{Ph})_4]_2$ , (I), which was obtained from the hexafluorophosphate salt, exchanging  $\text{PF}_6^-$  for  $[\text{B}(\text{Ph})_4]^-$ . The asymmetric unit of (I) contains one tetraphenylborate anion and half a  $[\{\text{Ni}(\text{dien})(\text{H}_2\text{O})\}_2(\text{ox})]^{2+}$  complex cation, which has an inversion centre at the mid-point of the C—C bond of the oxalate.

The  $[\{\text{Ni}(\text{dien})(\text{H}_2\text{O})\}_2(\text{ox})]^{2+}$  complex cation consists of two  $\text{Ni}^{\text{II}}$  atoms bridged by an oxalate ligand in the usual bis-



**Figure 1**  
View of (I) (50% probability displacement ellipsoids). H atoms on C atoms have been omitted for clarity.



**Figure 2**  
(a) View of the crystal packing along the *b* axis, highlighting the alternating cationic and anionic layers, and (b) a detailed view of the interaction between water molecules and phenyl rings.

bidentate fashion. The coordination geometry around each Ni<sup>II</sup> is distorted NiN<sub>3</sub>O<sub>3</sub> octahedral, with two O atoms from opposite ends of the oxalate bridge and the terminal N atoms of the dien ligand in the equatorial plane. The axial positions are occupied by a water molecule and the central N atom of the dien ligand, in such a way that the dien shows a *fac* arrangement. The tetraphenylborate shows the usual tetrahedral coordination around the B atom.

The title compound displays a two-dimensional arrangement. The complex cations and tetraphenylborate anions are situated in alternate layers that pack along the [10 $\bar{1}$ ] direction (Fig. 2) in such a way that three phenyl rings of the anions are embedded in the cationic layers, two of them (rings C11–C16 and C31–C36) forming O–H $\cdots\pi$  interactions with the axial water molecules (Table 2).

## Experimental

A solution containing 23.4 mg of sodium tetraphenylborate in 8 ml of water was added to a solution of 25.1 mg of [(Ni(dien)-(H<sub>2</sub>O)<sub>2</sub>(ox)](PF<sub>6</sub>)<sub>2</sub> in 11 ml of water and a blue precipitate was formed. The title compound was obtained upon recrystallization of this precipitate from ethanol. Elemental analysis(%): found (C, H, N)

64.39, 6.48, 7.77; calculated for C<sub>58</sub>H<sub>70</sub>B<sub>2</sub>N<sub>6</sub>Ni<sub>2</sub>O<sub>6</sub>: 64.13, 6.50, 7.74. IR (cm<sup>-1</sup>): 3227, 3209, 1643, 744, 714.

## Crystal data

[Ni<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)(C<sub>4</sub>H<sub>13</sub>N<sub>3</sub>)<sub>2</sub>(-H<sub>2</sub>O)<sub>2</sub>](C<sub>24</sub>H<sub>20</sub>B)<sub>2</sub>  
*M<sub>r</sub>* = 1086.24  
 Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 10.850 (1) Å  
*b* = 19.576 (3) Å  
*c* = 13.020 (2) Å  
 $\beta$  = 98.52 (1)°  
*V* = 2734.9 (6) Å<sup>3</sup>  
*Z* = 2

*D<sub>x</sub>* = 1.319 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 25 reflections  
 $\theta$  = 9.6–12.3°  
 $\mu$  = 0.74 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Prism, blue  
 0.50 × 0.30 × 0.25 mm

## Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\omega/2\theta$  scans  
 8287 measured reflections  
 7975 independent reflections  
 4921 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.046

$\theta_{\max}$  = 30.0°  
*h* = -15 → 15  
*k* = 0 → 27  
*l* = 0 → 18  
 2 standard reflections every 100 reflections  
 intensity decay: 4%

## Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.045  
*wR*(*F*<sup>2</sup>) = 0.126  
*S* = 1.01  
 7975 reflections  
 343 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.057P)^2 + 0.7675P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.43 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.50 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Ni1–O1	2.065 (2)	Ni1–N7	2.078 (2)
Ni1–O2	2.067 (2)	B1–C11	1.647 (3)
Ni1–O3	2.095 (2)	B1–C21	1.629 (3)
Ni1–N1	2.088 (2)	B1–C31	1.642 (3)
Ni1–N4	2.085 (2)	B1–C41	1.641 (3)
O2–Ni1–N1	86.53 (8)	N4–Ni1–O3	169.72 (9)
N7–Ni1–N1	103.43 (9)	C21–B1–C41	102.84 (17)
N4–Ni1–N1	82.80 (9)	C21–B1–C31	110.37 (18)
O1–Ni1–O3	92.47 (8)	C21–B1–C11	116.13 (19)
O2–Ni1–O3	90.31 (8)	C31–B1–C11	102.93 (17)
N7–Ni1–O3	90.66 (9)	C41–B1–C31	114.38 (18)
N1–Ni1–O3	90.61 (9)	C41–B1–C11	110.63 (18)

**Table 2**

Geometrical parameters (Å, °) of the O–H $\cdots\pi$  interactions.

O–H $\cdots\pi$	O–H	H $\cdots\pi$	O $\cdots\pi$	O–H $\cdots\pi$
O3–H31w $\cdots$ Cg1 <sup>a</sup>	0.78 (4)	2.42 (4)	3.168 (3)	161 (3)
O3–H32w $\cdots$ Cg3 <sup>b</sup>	0.76 (3)	2.47 (3)	3.192 (2)	158 (4)

Notes: (a) Cg1 is the centroid of phenyl ring C11<sup>i</sup>–C16<sup>i</sup>; (b) Cg3 is the centroid of phenyl ring C31<sup>i</sup>–C36<sup>i</sup>. Symmetry code: (i) -*x*, -*y*, 1 - *z*.

The H atoms of the water molecule and amino groups of the dien ligand were located in a Fourier difference map. The positions of all remaining H atoms were calculated geometrically. Water H atoms were refined freely. All remaining H atoms were refined as riding, with isotropic displacement parameters fixed at 1.2 times the equivalent isotropic displacement parameters of their parent atoms. The N–H distance was refined, while the C–H distances were fixed at ideal values.

Data collection: *CAD-4 EXPRESS* (Enraf-Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *DIRDIF99.2* (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* for Windows (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2002); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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## References

- Beurskens, P. T., Beurskens, G., de Gelder, R., García-Granda, S., Gould, R. O., Israel, R. & Smits, J. M. M. (1999). *The DIRDIF99 Program System*. Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.
- Brandenburg, K. (2002). *DIAMOND*. Version 2.1e. Crystal Impact GbR, Bonn, Germany.
- Cano, J., Ruiz, E., Alemany, P., Lloret, F. & Álvarez, S. (1999). *J. Chem. Soc. Dalton Trans.* pp. 1669–1676.
- Enraf-Nonius (1994). *CAD-4 EXPRESS Software*. Enraf-Nonius, Delft, The Netherlands.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Guzmán, C., Castillo, O., Luque, A., Beitia, J. I. & Román, P. (2001). *Acta Cryst. E57*, m407–m409.
- Harms, K. & Wocadlo, S. (1995). *XCAD4*. University of Marburg, Germany.
- Khan, O. (1993). *Molecular Magnetism*. New York: VCH.
- Muga, I., Gutiérrez-Zorrilla, J. M., Luque, A., Román, P. & Lloret, F. (1997). *Inorg. Chem.* **36**, 743–745.
- Muga, I., Gutiérrez-Zorrilla, J. M., Vitoria, P., Luque, A., Insausti, M., Román, P. & Lloret, F. (2000). *Eur. J. Inorg. Chem.* pp. 2541–2547.
- Muga, I., Vitoria, P., Gutiérrez-Zorrilla, J. M., Luque, A., Guzmán-Miralles, C. & Román, P. (2002). *Acta Cryst. C58*, m81–m83.
- Román, P., Guzmán-Miralles, C., Luque, A., Beitia, J. I., Cano, J., Lloret, F., Julve, M. & Álvarez, S. (1996). *Inorg. Chem.* **35**, 3741–3751.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Travnicek, Z., Smekal, Z. & Marek, J. (1997). *Z. Kristallogr.* **212**, 123–124.
- Vitoria, P., Muga, I., Gutiérrez-Zorrilla, J. M., Luque, A., Román, P., Lezama, L., Zuñiga, F. J. & Beitia, J. I. (2003). *Inorg. Chem.* **42**, 960–969.