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Two new $[Ni(tren)_2]^{2+}$ complexes: $[Ni(tren)_2]Cl_2$ and $[Ni(tren)_2]WS_4$

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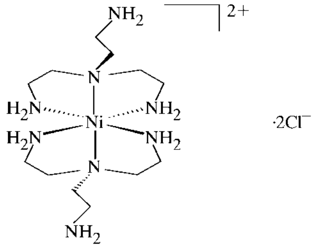
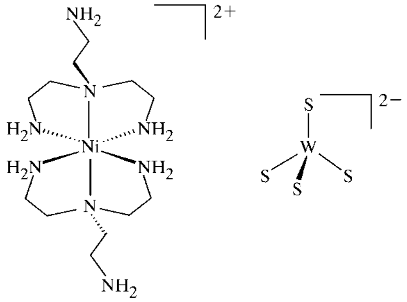
Both title compounds, bis[tris(2-aminoethyl)amine]nickel(II) dichloride, $[Ni(tren)_2]Cl_2$, (I), and bis[tris(2-aminoethyl)-amine]nickel(II) tetrathiotungstate, $[Ni(tren)_2]WS_4$, (II), contain the $[Ni(tren)_2]^{2+}$ cation [tren is tris(2-aminoethyl)-amine, $C_6H_{18}N_4$]. The tren molecule acts as a tridentate ligand around the central Ni atom, with the remaining primary amine group not bound to the central atom. In (I), Ni^{2+} is located on a centre of inversion surrounded by one crystallographically independent tren molecule. In the $[Ni(tren)_2]^{2+}$ cation of (II), the Ni atom is bound to two crystallographically independent tren molecules. The Ni atoms in the $[Ni(tren)_2]^{2+}$ complexes are in a distorted octahedral environment consisting of six N atoms from the chelating tren molecules. The counter-ions are chloride anions in (I) and the tetrahedral $[WS_4]^{2-}$ anion in (II). Hydrogen bonding is observed in both compounds.

Comment

It is well documented that the tren molecule can act as a tri- or tetradentate ligand and several transition metal complexes have been prepared (Gaudin *et al.*, 1986). Many transition metal ions prefer octahedral geometry with tren as a tetradentate ligand, leaving two *cis* positions available for bonding to other ligands; examples are $[Ni(tren)(H_2O)Cl]Cl\cdot H_2O$ (Marzotto *et al.*, 1993) and $[Ni(tren)\{N(CN)_2\}_2]$ (Březina *et al.*, 1999). If the two *cis* positions are used by another multidentate ligand, such as the oxalate anion, dimeric complexes were obtained, with the two Ni(tren) units bridged by the other multidentate ligand, as in $[Ni_2(tren)_2(C_2O_4)](ClO_4)_2$ (Castro *et al.*, 1997; Březina *et al.*, 1997) and $[Ni_2(tren)_2(C_6O_4Cl_2)](BPh_4)_2$ (Pierpont *et al.*, 1977). Another binding mode of the tren ligand yields cationic chains. These chains are found in the two compounds $\{[Ni_2(tren)_3](ClO_4)_4\cdot H_2O\}_n$ (Masters *et al.*, 1999) and $\{[Ni_2(tren)_3][Mo_2O_2S_6]_2\cdot 2.75H_2O\}_n$ (Ellermeier & Bensch, 2001). In the polymeric chains, one Ni atom is coordinated by two tren molecules, which act as tridentate ligands. The other Ni atom is coordinated by all four N atoms of one tren molecule and by the two remaining N atoms of the two tren ligands which are tridentate to the neighbouring Ni atoms. The coordination behaviour of the tren molecules leads to the formation of zigzag $[Ni_2(tren)_3]_n$ chains. The two new $[Ni(tren)_2]^{2+}$ complexes presented here contain isolated cations, with the tren molecules acting as tridentate ligands. This coordination mode was first reported by Colpas *et al.* (1990) for $[Ni(tren)_2](BF_4)_2$.



(I)



(II)

Violet crystals of $[Ni(tren)_2]Cl_2$, (I), were obtained during attempts to synthesize compounds which could be used as precursors for the syntheses of new thioantimonates with complex transition metal cations (Stähler & Bensch, 2001).

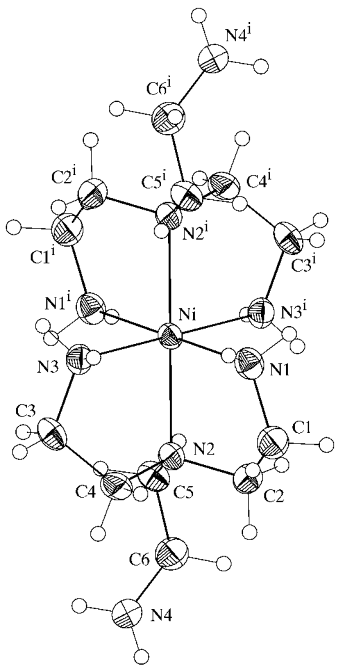


Figure 1
A view of the $[Ni(tren)_2]^{2+}$ cation in (I) with the atom-labelling scheme and displacement ellipsoids drawn at the 50% probability level [symmetry code: (i) $-x, 1-y, 1-z$].

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Due to the above-mentioned variety in the bonding modes of the multidentate tren molecule, a single-crystal diffraction study was performed. In contrast, $[Ni(tren)_2]WS_4$, (II), was obtained as part of a project on the synthesis of new thiotungstates with transition metals under solvothermal conditions. Both compounds contain the $[Ni(tren)_2]^{2+}$ complex cation, and the counter-ions are Cl^- in (I) and the tetrahedral $[WS_4]^{2-}$ anion in (II). Each Ni^{2+} cation in $[Ni(tren)_2]^{2+}$ in (I) and (II) is sixfold coordinated by the N atoms of two tren molecules acting as tridentate ligands. Therefore, each tren ligand has one primary amine group which is not connected to the transition metal atom. The structures of the cations in (I) and (II) are illustrated in Figs. 1 and 2, and selected bond lengths and angles are given in Tables 1 and 3, respectively. In (I), the Ni atom is on a centre of inversion, surrounded by one crystallographically independent tren molecule. The environment is completed by a tren molecule generated by symmetry. In (II), the Ni atom is bound to two crystallographically independent tren molecules. The Ni—N bond lengths in (I) are between 2.105 (3) and 2.176 (3) Å. The N—Ni—N angles range from 80.56 (11) to 99.44 (11)°, reflecting the distortion of the octahedral geometry. The chloride anions in (I) are involved in a complicated hydrogen-bond network (Table 2) that may contribute significantly to the stability of the compound. There are five short intermolecular contacts between the Cl^- anions and the H atoms of the tren ligand ranging from 2.40 (4) [$H3N\cdots Cl^{ii}$; symmetry code: (ii) $-x, -y, -z$] to 2.61 (4) Å ($H2N\cdots Cl^{ii}$). A short contact is also observed between an H atom and an N atom of a neighbouring tren molecule [$H4N\cdots N4^{iii}$; symmetry code: (iii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$].

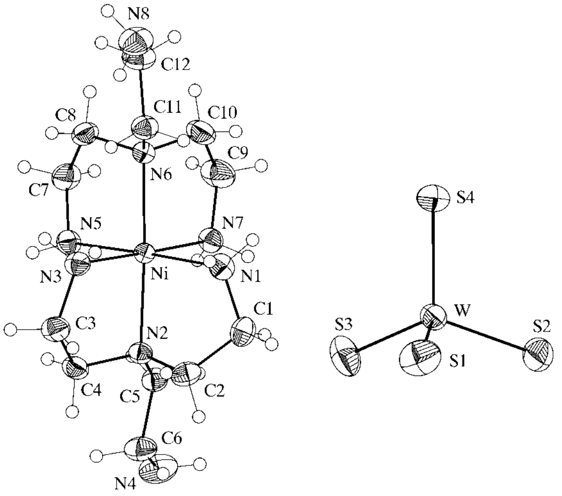

Figure 2

The crystal structure of the anion and cation in $[Ni(tren)_2]WS_4$, (II), showing the atom-labelling scheme and displacement ellipsoids drawn at the 50% probability level.

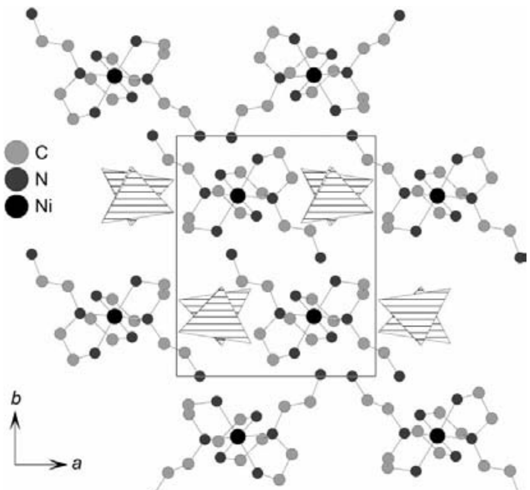

Figure 3

The packing diagram for (II), viewed along the *c* axis. H atoms have been omitted for clarity.

The WS_4 tetrahedron in compound (II) is only slightly distorted (Fig. 2), with S—W—S angles between 108.39 (4) and 110.78 (4)° (Table 3). The W—S bond lengths range from 2.1580 (10) to 2.2122 (9) Å. The W—S3 distance of 2.2122 (9) Å is significantly longer than the average W—S bond length in $[WS_4]^{2-}$ anions of 2.177 Å (Müller *et al.*, 1981). One reason may be that S3 is involved in three short contacts to H atoms of the tren ligands (Table 4). The other S atoms have only one relatively short contact to H atoms. The geometrical parameters for the $[Ni(tren)_2]^{2+}$ cation in (II) are in good agreement with that found in the cation of (I) and the $[Ni(tren)_2]^{2+}$ cation described by Colpas *et al.* (1990). The Ni—N bond lengths vary from 2.130 (3) to 2.152 (2) Å and the corresponding *cis*-N—Ni—N angles range from 80.95 (10) to 100.13 (10)° (Table 3). The $[WS_4]^{2-}$ anions and $[Ni(tren)_2]^{2+}$ cations in (II) each form rods along the *a* and *c* axes, and the rods alternate along the *b* axis (Fig. 3).

Experimental

$[Ni(tren)_2]Cl_2$, (I), was prepared in a 100 ml glass flask at room temperature (293 K). $NiCl_2\cdot 6H_2O$ (237.7 mg, 1 mmol) was dissolved in ethanol (99%, 10 ml) and tren (95%, 10 ml) was added to the mixture. Violet crystals were obtained after 48 h. The phase-pure product was washed with ethanol and dried under vacuum. $[Ni(tren)_2]WS_4$, (II), was prepared under solvothermal conditions. $NiCl_2\cdot 6H_2O$ (0.50 mmol), $Na_2WO_4\cdot 2H_2O$ (1 mmol) and sulfur (4 mmol) were reacted in tris(2-aminoethyl)amine (95%, 3 ml) in a Teflon-lined steel autoclave at 393 K for 5 d. The product was filtered off and washed with water. The yield of the phase-pure product was about 60%. The yellow–brown crystals obtained were stable in air.

Compound (I)

Crystal data

$[Ni(C_6H_{18}N_4)_2]Cl_2$
$M_r = 422.10$
Monoclinic, $P2_1/n$
$a = 9.0336$ (18) Å
$b = 10.630$ (2) Å
$c = 10.717$ (2) Å
$\beta = 108.78$ (3)°
$V = 974.3$ (3) Å^3
$Z = 2$
$D_x = 1.439$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 37 reflections
$\theta = 9$–16°
$\mu = 1.28$ mm^{-1}
$T = 293$ (2) K
Needle, violet
0.5 × 0.1 × 0.1 mm

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Table 1
Selected geometric parameters (Å, °) for (I).

Ni—N1	2.152 (3)	Ni—N3	2.105 (3)
Ni—N2	2.176 (3)		
N1—Ni—N2	80.56 (11)	N3—Ni—N1	92.29 (11)
N1^{i}—Ni—N2	99.44 (11)	N3—Ni—N2	82.72 (10)
N3^{i}—Ni—N1	87.71 (11)	N3—Ni—N2^{i}	97.28 (10)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···Cl^{i}	0.91 (3)	2.60 (3)	3.475 (3)	162 (3)
N1—H2N···Cl^{ii}	0.84 (4)	2.61 (4)	3.402 (3)	159 (3)
N3—H3N···Cl^{ii}	0.89 (4)	2.40 (4)	3.284 (3)	172 (3)
N3—H4N···N4^{iii}	0.86 (3)	2.28 (3)	3.087 (4)	156 (3)
N4—H5N···Cl^{iv}	0.87 (4)	2.57 (4)	3.432 (3)	172 (4)
N4—H6N···Cl	0.90 (4)	2.51 (4)	3.406 (3)	172 (3)

Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (ii) $1-x, 1-y, 1-z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iv) $1-x, -y, 1-z$.

Data collection

Stoe AED-II four-circle diffractometer
ω–θ scans
Absorption correction: ψ scan [*X-SHAPE* (Stoe & Cie, 1998) and *X-RED* (Stoe & Cie, 1998)]
$T_{\min} = 0.810$, $T_{\max} = 0.840$
2042 measured reflections
1715 independent reflections
1131 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$
$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 10$
$k = -12 \rightarrow 1$
$l = -12 \rightarrow 12$
4 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.073$
$S = 1.01$
1715 reflections
160 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0306P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.28$ e Å^{-3}
$\Delta\rho_{\min} = -0.27$ e Å^{-3}

Compound (II)

Crystal data

$[Ni(C_6H_{18}N_4)_2]WS_4$
$M_r = 663.29$
Monoclinic, $P2_1/c$
$a = 10.147$ (2) Å
$b = 11.852$ (2) Å
$c = 19.122$ (4) Å
$\beta = 104.44$ (3)°
$V = 2227.1$ (8) Å^3
$Z = 4$
$D_x = 1.978$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 128 reflections
$\theta = 4$–20°
$\mu = 6.40$ mm^{-1}
$T = 293$ (2) K
Polyhedron, yellow–orange
0.20 × 0.08 × 0.04 mm

Data collection

Philips PW1100 four-circle diffractometer
ω–θ scans
Absorption correction: ψ scan [*X-SHAPE* (Stoe & Cie, 1998) and *X-RED* (Stoe & Cie, 1998)]
$T_{\min} = 0.358$, $T_{\max} = 0.463$
6750 measured reflections
5386 independent reflections
4522 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$
$\theta_{\max} = 28.0°$
$h = 0 \rightarrow 13$
$k = -15 \rightarrow 2$
$l = -25 \rightarrow 24$
4 standard reflections
frequency: 120 min
intensity decay: none

Table 3
Selected geometric parameters (Å, °) for (II).

W—S1	2.1580 (10)	Ni—N2	2.146 (2)
W—S2	2.1860 (9)	Ni—N3	2.138 (3)
W—S3	2.2122 (9)	Ni—N5	2.136 (3)
W—S4	2.1929 (9)	Ni—N6	2.152 (2)
Ni—N1	2.130 (3)	Ni—N7	2.143 (3)
S1—W—S2	108.39 (4)	N3—Ni—N2	80.95 (10)
S1—W—S3	110.78 (4)	N5—Ni—N2	95.56 (10)
S1—W—S4	108.75 (5)	N2—Ni—N6	177.05 (9)
S2—W—S3	109.68 (4)	N7—Ni—N2	100.13 (10)
S2—W—S4	109.24 (4)	N5—Ni—N3	88.79 (11)
S4—W—S3	109.97 (4)	N3—Ni—N6	96.42 (10)
N1—Ni—N2	82.75 (10)	N3—Ni—N7	178.78 (10)
N1—Ni—N3	92.96 (11)	N5—Ni—N6	83.01 (9)
N1—Ni—N5	177.34 (11)	N5—Ni—N7	90.54 (11)
N1—Ni—N6	98.77 (10)	N7—Ni—N6	82.49 (10)
N1—Ni—N7	87.74 (11)		

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···N8^{i}	0.87 (4)	2.52 (4)	3.358 (4)	161 (3)
N1—H2N···S3^{i}	0.83 (4)	2.75 (4)	3.565 (3)	171 (3)
N3—H3N···S3^{i}	0.89 (4)	2.87 (4)	3.747 (3)	169 (3)
N5—H7N···S2^{ii}	0.90 (4)	2.82 (4)	3.640 (3)	152 (3)
N5—H8N···S3^{iii}	0.86 (4)	2.73 (4)	3.562 (3)	162 (3)
N7—H9N···S1^{iv}	0.86 (4)	2.75 (4)	3.561 (3)	158 (3)
N7—H10N···S4^{ii}	0.80 (4)	2.76 (4)	3.528 (3)	162 (3)

Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $1-x, 1-y, 1-z$; (iii) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (iv) $1+x, y, z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.053$
$S = 1.03$
5386 reflections
343 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0246P)^2 + 1.1404P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.84$ e Å^{-3}
$\Delta\rho_{\min} = -0.65$ e Å^{-3}

The H atoms of both compounds were positioned with idealized geometry and were refined isotropically [C—H 0.80 (4)–1.08 (4) Å].

For both compounds, data collection: *DIF*4 (Stoe & Cie, 1992); cell refinement: *DIF*4; data reduction: *REDU*4 (Stoe & Cie, 1992); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Crystal Impact, 1999); software used to prepare material for publication: *CIFTAB* in *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1089). Services for accessing these data are described at the back of the journal.

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