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UNUSUAL COORDINATION OF TRIPODAL NN_3S_3 DONOR LIGAND WITH NICKEL(II): SINGLE CRYSTAL X-RAY STRUCTURE OF $[Ni\{H_2NCH_2CH_2N(CH_2CH_2N{=}CH(C_4H_3S))_2\}(CH_3CN)(H_2O)](PF_6)_2$

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Abstract—Reaction of $Ni(acetate)_2 \cdot 6H_2O$ with a potentially heptentate Schiff base ligand, tris[4-(2-thienyl)-3-aza-3-butenyl]amine [$(thiophene)_3tren$], resulted in the formation of an unexpected octahedral Ni^{II} complex with an NiN_4 core and the remaining two coordination sites occupied by solvent molecules. An X-ray crystal structure of the complex established the unusual cleavage at one of the three α-imino bonds and revealed that it deviates from the usual mono-capped trigonal prismatic coordination polyhedron designed for this type of complex. The complex molecule has an approximate plane of symmetry (C_s) rather than the three-fold axis (C_3) normally observed for this type of complex and is the first example where the apical 'unique' nitrogen approaches the Ni^{II} as closely as the other three nitrogens of the ligand.

Transition metal complexes of tripodal ligands and their derivatives have been extensively investigated as these complexes exhibit 'special' physical, chemical and structural properties.[1] Moreover, they may serve as candidates for magnetic resonance imaging agents.[2] The most widely used tripodal ligands are condensation products of tren, $[N(CH_2CH_2NH_2)_3]$, and an aldehyde, e.g. 2-pyridinecarboxaldehyde, 2-pyrrolecarboxaldehyde or salicylaldehyde. The ligand, $(py)_3tren$ (py = 2-pyridinecarboxaldehyde) with its three-fold symmetry and unique placement of its apical donor nitrogen atom, should result in complexes exhibiting mono-capped trigonal antiprismatic coordination with distortion towards a trigonal prism (as the distance between the metal and apical nitrogen atom is long, >2.79 Å, and is greater than the sum of the van der Waals radii).[1] A recent report on hepta-coordinated complexes of Co^{II} and Ni^{II} using $(pyo)_3tren$ (pyo = 2-pyridinecarboxaldehyde-*N*-oxide) as the coordinating ligand showed a significantly longer $M—N_{apical}$ distance (>2.44 Å) compared to the three equivalent $M—N_{imino}$ distances (<2.27 Å).[3] While in the case of $(sal)_3tren$ (sal = salicylaldehyde), the apical nitrogen atom does not take part in the coordination to the metal centre.[4,5] However, to date, little is known about the coordination chemistry of the potentially heptadentate NN_3S_3 donor ligand, $(thiophene)_3tren$ (**1**).[6] Hence we report herein the unusual complexation of $Ni(acetate)_2 \cdot 6H_2O$ with $(thiophene)_3tren$.

EXPERIMENTAL

The $Ni(acetate)_2 \cdot 6H_2O$, NH_4PF_6, tren and 2-thiophenecarboxaldehyde used were of commercial grade and were used without purification. Absorption spectra were recorded with a Shimadzu 160 UV–vis spectrometer. IR spectra were recorded on a Carl Zeiss Specord M80 spectrometer as KBr pellets. ^1H NMR spectra were recorded in CD_2Cl_2 using a JEOL 100 FT-NMR instrument. Electron-

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✠ Deceased.

Table 1. Crystal data

$[Ni(C_{18}H_{25}N_5OS_2)](PF_6)_2$
$M_r = 740.2$
Monoclinic
$P2_1/n$
$a = 9.180(3)$ Å
$b = 27.309(6)$ Å
$c = 12.042(4)$ Å
$\beta = 101.25(2)$
$V = 2961(3)$ Å^3
$Z = 4$

$D_x = 1.660$ Mg m^{-3}
Mo-K_α radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections with $\theta_{max} = 12^\circ$
$\mu = 9.955$ cm^{-1}
$T = 295$ K
Light violet
$0.30 \times 0.20 \times 0.10$ mm

Data collection
Enraf–Nonius CAD-4 diffractometer
$\omega - 2\theta$ scan mode
Absorption correction: empirical[7]

$T_{min} = 95\%$, $T_{max} = 99.9\%$
4363 measured reflections
2786 observed reflections
$[I \geqslant 3\sigma(I)]$

$\theta_{max} = 23.5^\circ$
$h = 0$–10
$k = 0$–30
$l = -13$ to 13
Three standard reflections
Frequency = 60 min
No significant variation

Refinement
Refinement on $|F|$
$R = 0.064$
$R_w = 0.065$
$S = 1.80$
2786 reflections
370 parameters

(δ/σ) max = 0.03
$\delta\rho_{max} = 0.6$ e Å^{-3}
$\delta\rho_{min} = -0.8$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. 4)

impact mass spectra were recorded on a Kratos MS9 instrument. Electrochemical measurements were performed using a PAR 174A potentiostat. All cyclic voltammetric experiments were carried out in CH_3CN, freshly distilled from CaH_2, using a platinum working electrode. Potentials are reported with respect to the ferrocene/ferrocenium couple.

Synthesis

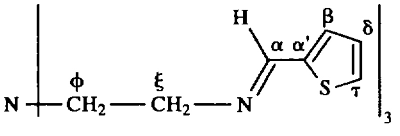
Tren and 2-thiophene carboxaldehyde in 1:3 molar ratio were allowed to react in ethanol for 30 min at room temperature. The reaction mixture was filtered and the solid residue was recrystallized from hot ethanol to afford pure ligand (**1**) as a pale yellow powder. EI-MS: *m/z* 428 (M^+, 100%). ^1H NMR: 8.16 (3H, s, N═CH), 7.35 (3H, d, $J = 4.3$ Hz, τH), 7.02 (3H, t, $J = 4.3$ Hz, δH), 6.88 (3H, d, $J = 4.1$ Hz, βH) 3.56 (6H, t, $J = 5.86$ Hz, εH), 2.81 (6H, z, $J = 5.86$ Hz, ϕH). Found: C, 58.9; H, 5.6; N, 13.0. Calc. for $C_{21}H_{24}N_4S_3$: C, 58.8; H, 5.6; N, 13.1%. The corresponding nickel complex was synthesized by heating an equimolar mixture of ligand (**1**; 428 mg, 1 mM) and $Ni(acetate)_2 \cdot 6H_2O$ (285 mg, 1 mM) dissolved in CH_3OH, on a water bath with constant stirring for 45 min. NH_4PF_6 was then added in a little excess with further stirring for 5–10 min and then filtered hot. The volume of the filtrate was reduced to 10 cm^3 and upon cooling, a pale purple coloured Ni^{II} complex was precipitated which was further recrystallized from CH_3CN–C_2H_5OH. Yield: 340 mg, 45%. Found: C, 32.0; H, 3.9; N, 10.1%.

Structural analysis

Crystallographic data for complex **1** are given in Table 1. The structure was solved by the heavy-atom method and refined by full-matrix least-square procedures as summarized in Table 1. The hydrogen atom positions were mostly obtained from difference Fourier synthesis; a few were fixed stereochemically at appropriate geometries. The hydrogen atoms were included only for the structure factor calculation and were not refined by least-squares procedures. All computations were performed on a PDP-11/73 computer using a structure determination package available from Enraf–Nonius.[8]

RESULTS AND DISCUSSION

Complete condensation of tren with 2-thiophenecarboxaldehyde was confirmed by mass spectral analysis, IR (no characteristic band was observed for the free —NH_2 group), ^1H NMR spectroscopy and also by elemental analysis.



Structure of ligand 1

Complex **1** was isolated as the hexafluorophosphate salt and was expected to have an octahedral geometry utilizing three N_{imino} and three $S_{thiophene}$ atoms for coordination to the Ni^{II} centre. However, the elemental analysis data did not match with those calculated for $[Ni(thiophene)_3tren](PF_6)_2$ (C, 32.4; H, 3.1; N, 7.2%). The Ni^{II} complex is paramagnetic but no EPR signal could be obtained. Since Ni^{II} is not a Kramers ion, the zero field splitting can be large enough to lift the whole three-fold spin degeneracy of the ground state, and may not give an EPR signal.[9] Electronic spectra of the complex exhibit three absorption bands at 375 (ε: 335 M^{-1} cm^{-1}), 543 (ε: 32 M^{-1} cm^{-1}) and 898 nm (ε: 38 M^{-1} cm^{-1}), which can be assigned in O_h symmetry to $^3A_2g \rightarrow {}^3T_2g$, $^3A_2g \rightarrow {}^3T_1g$ and $^3A_2g \rightarrow {}^3T_1g(P)$ transitions, respectively and is very similar to the typical $Ni^{II}N_6$ or $Ni^{II}N_5X$ (X = O, Cl etc.) type chromophore.[9,10] CV studies of complex **1** exhibit two quasi-reversible couples, one at $E_{1/2} = +0.63$ V ($\Delta E_p = 190$ mV) for the $Ni^{3+/2+}$ couple and the other one at $E_{1/2} = -1.85$ V ($\Delta E_p = 220$ mV) for the $Ni^{2+/+}$ couple. The $E_{1/2}$ values obtained could not confirm whether or not thiophene unit(s) were involved in coordination to the Ni^{II} centre. The IR spectra of the complex showed coordination of the N_{imino} atoms [as ν(C=N) in the free ligand is shifted from 1635 to 1620 cm^{-1} in the Ni^{II} complex].[11] Moreover, two additional bands at 3280 (m) and 1610 (s) cm^{-1} (indicative of a coordinated —NH_2 group[11]) and a broad band at 3400 cm^{-1} appeared. An explanation for this apparently anomalous observation (mismatch of the elemental analysis data and presence of bands in the IR spectrum corresponding to a coordinated —NH_2 group) was provided by structural analysis.

An ORTEP[12] view of the molecule **1** along with the atom numbering is shown in Fig. 1. The crystal structure confirmed the cleavage at one of the three α-imino groups. As a consequence, the ligand has adopted an approximate plane of symmetry upon complex formation [a mirror may be imagined passing through N(1), Ni, N(4) and C(15) bisecting the molecule in two almost equal halves]. This is probably the first example of this geometry with this type of ligand, which deviates from its usual polyhedron possessing three-fold symmetry.[1] The Ni^{II} centre has somewhat distorted octahedral geometry (Table 2); out of the six coordination sites, four are provided by the nitrogens of the ligand and the remaining two by acetonitrile and water molecules. None of the sulphur atoms of the two thiophene

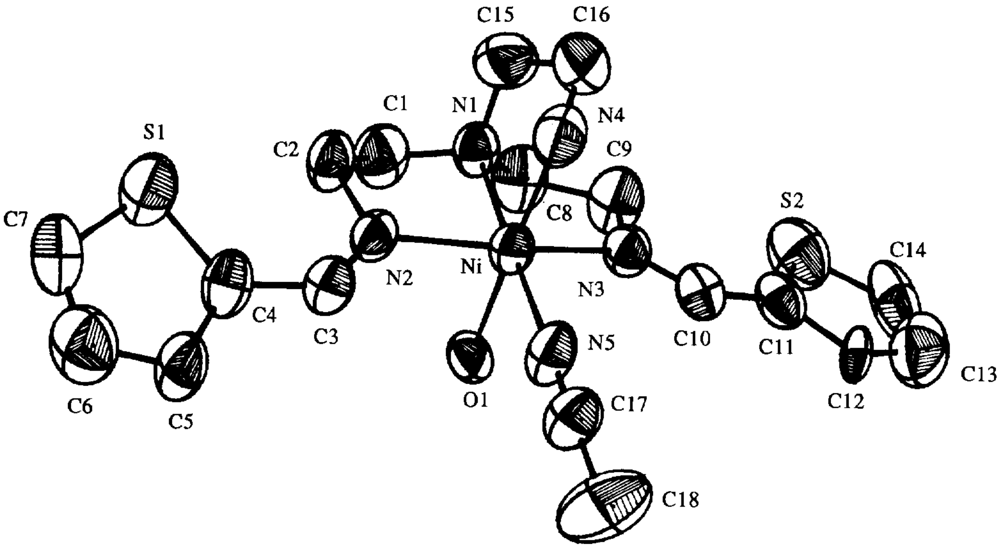


Fig. 1. ORTEP view of $[Ni(H_2NCH_2CH_2N(CH_2CH_2N{=}CH(C_4H_3S))_2)(CH_3CN)(H_2O)]^{2+}$ with atom numbering.

Table 2. Bond distances (Å) and bond angles (°)

Ni(1)—N(1)	2.077(7)	Ni(1)—N(2)	2.078(6)	Ni(1)—N(3)	2.076(6)
Ni(1)—N(4)	2.067(8)	Ni(1)—N(5)	2.062(8)	Ni(1)—O(1)	2.152(7)
S(1)—C(4)	1.72(1)	S(1)—C(7)	1.68(2)	S(2)—C(11)	1.70(1)
S(2)—C(14)	1.68(1)	N(1)—C(1)	1.47(2)	N(1)—C(8)	1.48(1)
N(1)—C(15)	1.46(1)	N(2)—C(2)	1.48(1)	N(2)—C(3)	1.27(1)
N(3)—C(9)	1.47(1)	N(3)—C(10)	1.27(2)	N(4)—C(16)	1.51(1)
N(5)—C(17)	1.13(1)	C(1)—C(2)	1.53(1)	C(3)—C4	1.47(2)
C(4)—C(5)	1.42(1)	C(5)—C(6)	1.38(1)	C(6)—C(7)	1.34(2)
C(8)—C(9)	1.54(1)	C(10)—C(11)	1.45(2)	C(11)—C(12)	1.43(1)
C(12)—C(13)	1.38(1)	C(13)—C(14)	1.31(2)	C(15)—C(16)	1.52(2)
C(17)—C(18)	1.46(2)				
N(1)—Ni(1)—N(2)	83.3(3)	N(1)—Ni(1)—N(3)	82.2(3)	N(1)—Ni(1)—N(4)	85.0(3)
N(1)—Ni(1)—N(5)	179.4(2)	N(1)—Ni(1)—O(1)	93.8(3)	N(2)—Ni(1)—N(3)	163.3(3)
N(2)—Ni(1)—N(4)	95.2(3)	N(2)—Ni(1)—N(5)	97.3(3)	N(2)—Ni(1)—O(1)	87.3(3)
N(3)—Ni(1)—N(4)	91.9(3)	N(3)—Ni(1)—N(5)	97.2(3)	N(3)—Ni(1)—O(1)	85.3(3)
N(4)—Ni(1)—N(5)	94.9(3)	N(4)—Ni(1)—O(1)	177.0(3)	N(5)—Ni(1)—O(1)	86.3(3)
C(4)—S(1)—C(7)	90.9(5)	C(11)—S(2)—C(14)	91.1(5)	Ni(1)—N(1)—C(1)	106.4(6)
Ni(1)—N(1)—C(8)	105.2(6)	Ni(1)—N(1)—C(15)	109.4(7)	C(1)—N(1)—C(8)	109.3(7)
C(1)—N(1)—C(15)	113.7(7)	C(8)—N(1)—C(15)	112.4(8)	Ni(1)—N(2)—C(2)	110.3(5)
Ni(1)—N(2)—C(3)	126.7(5)	C(2)—N(2)—C(3)	123.1(6)	Ni(1)—N(3)—C(9)	112.5(5)
Ni(1)—N(3)—C(10)	126.5(6)	C(9)—N(3)—C(10)	121.1(7)	Ni(1)—N(4)—C(16)	104.7(6)
Ni(1)—N(5)—C(17)	175.3(9)	N(1)—C(1)—C(2)	109.9(8)	N(2)—C(2)—C(1)	108.6(7)
N(2)—C(3)—C(4)	132.2(8)	S(1)—C(4)—C(3)	126.6(7)	S(1)—C(4)—C(5)	111.2(6)
C(3)—C(4)—C(5)	122.1(8)	C(4)—C(5)—C(6)	110.0(9)	C(5)—C(6)—C(7)	115.0(2)
S(1)—C(7)—C(6)	113.3(7)	N(1)—C(8)—C(9)	110.2(8)	N(3)—C(9)—C(8)	109.9(8)
N(3)—C(10)—C(11)	132.6(9)	S(2)—C(11)—C(10)	127.3(7)	S(2)—C(11)—C(12)	110.3(6)
C(10)—C(11)—C(12)	122.4(9)	C(11)—C(12)—C(13)	110.3(8)	C(12)—C(13)—C(14)	114.0(1)
S(2)—C(14)—C(13)	114.6(9)	N(1)—C(15)—C(16)	112.9(8)	N(4)—C(16)—C(15)	110.0(8)
N(5)—C(17)—C(18)	179(2)				

Numbers in parenthesis are estimated standard deviations in the least significant digits.

units take part in the coordination. The nitrogen N(1) is perpendicular to the remaining three nitrogens N(2), N(3) and N(4) of the ligand and *trans* to the acetonitrile nitrogen, N(5), with Ni^{II}—N distances being almost equal [Ni—N (av.) = 2.072(6) Å; Table 2]. It is noteworthy that in all other instances the apical nitrogen atom of $(py)_3$tren and $(sal)_3$tren ligands is either not involved in the coordination to the metal centre or if coordinated, the $M—N_{apical}$ distance is much longer than that of $M—N_{imino}$.[1,3–6,13] Thus, it is a unique example where the apical nitrogen, N(1), has been able to approach the Ni^{II} ion as closely as the other three nitrogens. The sixth coordination from water, however, is longer [Ni—O(H_2O) = 2.152(7) Å] than the Ni—N bonds. The acetonitrile is coordinated in a linear fashion, with N(5)—C(17)—C(18) = 179(2)°, as expected for this group.

All three five-membered rings (involving three ethylene diamine units) are in an 'envelope' conformation and their envelope head atoms C(1), C(8) and C(16) are not situated symmetrically with respect to the apical nitrogen, N(1). The carbon atoms C(1), C(8) and C(16) are away from the least-squares plane containing Ni—N(1)—N(2)—C(2), Ni—N(1)—N(3)—C(9) and Ni—N(1)—N(4)—C(15) by ≈0.6 Å, respectively. Structural studies on the Ni^{II} complex have thus clearly established an unusual cleavage at one of the three imino bonds. Similar cleavage was also reported earlier but instances are very rare.[1] The most plausible explanation for this cleavage is hydrolysis. However, it is difficult to ascertain whether the hydrolysis occurred during complex synthesis or recrystallization. Thus, in this instance, CH_3CN and H_2O are stronger nucleophiles than thiophene. The non-coordinating nature of the thiophene has also been reported[14] for the reaction of ZnX_2 (X = Cl, Br, I) with the neutral ligand bis(pyrazolyl)(thiophene) methane. To the best of our knowledge, it is the second crystal structure for this type of hydrolysed product. Moreover, the present structure is the first reported example of the unusual binding mode of this type of tripodal Schiff base ligand, where the M—N(1) bond is as strong as the $M—N_{imino}$ bonds.

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