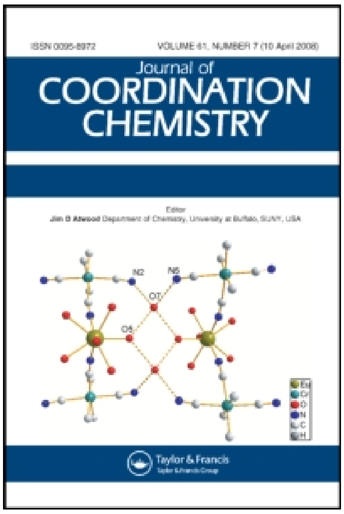

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SYNTHESIS AND CRYSTAL STRUCTURE OF NICKEL COMPLEX WITH TRIS(3-AMINOPROPYL)AMINE

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The crystal structure of [Ni(trpn)(NCS)$_2$] (trpn = tris(3-aminopropyl)amine) has been determined, in which the nickel(II) complex is octahedral. The complex forms a three-dimensional network through weak intermolecular hydrogen bonds $S_{NCS} \cdots H{-}N_{amine}$ and $S \cdots S$ contacts.

Keywords: Tris(3-aminopropyl)amine; nickel(II); crystal structure

INTRODUCTION

Transition metal complexes of tripodal amine ligands are of value in catalytic studies and as intermediates in the synthesis of macrocyclic ligands.[1] There is a limited number of tripodal amine ligands; important examples are [N(CH$_2$CH$_2$NH$_2$)$_3$] (tren) and [N(CH$_2$CH$_2$CH$_2$NH$_2$)$_3$] (trpn). Structural research on complexes with tren has been continuing, wih the aim of studying magnetic behaviour in relation to structure.[2,3] With the nickel(II) complex [Ni(tren)(NCS)$_2$], an octahedral structure has been ascertained by X-ray analysis.[4] Herein we report the synthesis and crystal structure of a nickel(II) complex with trpn, [Ni(trpn)(NCS)$_2$]. It is interesting that a three-dimensional network of monomers was formed through weak intermolecular hydrogen bonds $S_{NCS} \cdots H{-}N_{amine}$ and $S \cdots S$ contacts.

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EXPERIMENTAL

Preparation

Trpn was prepared by a literature method.[5] Its physical constants and spectroscopic data were in agreement with literature values. An ethanol solution (10.0 cm^3) containing trpn (0.188 g, 1.00 mmol) was added dropwise to a stirred mixed solution of 0.213 g (2.20 mmol) of potassium thiocyanate and 0.402 g (1.10 mmol) of $Ni(ClO_4)_2 \cdot 6H_2O$ in 20.0 cm^3 of ethanol. After refluxing the mixture for 3 h, the resulting violet-blue precipitate was filtered off and dried under vacuum to give $[Ni(trpn)(NCS)_2]$ in 58% yield. The filtered solution was diffused by diethylether over one week and prismatic crystals suitable for X-ray diffraction were isolated. Nitrogen, carbon and hydrogen were analysed with a Carlo Erba 1160 instrument. *Anal.* calcd. for $C_{11}H_{24}N_6NiS_2$ (%): C 36.36, H 6.61, N 23.14. Found: C 36.42, H 6.53, N 23.35.

Crystal Structure Determination

A purple prismatic crystal with dimensions $0.40 \times 0.20 \times 0.15$ mm was mounted on a glass fibre and used for the structure determination. The intensities were collected at 293 K on a Siemens P4 diffractometer using the $\omega/2\theta$ scan mode with a variable scan speed 5.5°–50.0° min^{-1} (in ω). Some 4152 reflections (2816 unique, 1923 observed $[I > 2\sigma(I)]$) were collected in the range $1.95° < \theta < 25.00°$ with $R_{int} = 0.0505$. The data were corrected for Lorentz and polarization effects during data reduction using XSCANS.[6]

The crystal structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods. The C(2) atom (site occupancy factor (sof) for C(2) and C(2′) fixed at 0.67 and 0.33, respectively) was found to be disordered. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in a difference Fourier map. The contributions of these hydrogen atoms were included in the final structure factor calculations. The weighing scheme was $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $3P = (2F_c^2 + F_o^2)$ and a and b are constants adjusted by the program. The final R_w was 0.132, with conventional $R = 0.051$ and goodness-of-fit 0.977. All computations were carried out on a PC-586 using the SHELXTL program package.[7] Full lists of crystallographic data are available from the authors upon request.

Electrospray Mass Spectrum

Positive ion ES-MS was determined on a Finnigan LCQ mass spectrometer. The mobile phase was methanol; concentration of sample in methanol was about 10^{-4} mol dm^{-3}; diluted solution was electrosprayed at a flow rate of 5×10^{-6} dm^3 min^{-1} with needle voltage +4.5 kV.

RESULTS AND DISCUSSION

Crystal Structure

Crystal data for [Ni(trpn)(NCS)$_2$]: $C_{11}H_{24}N_6NiS_2$, $M = 363.19$, monoclinic, space group $P2_1/c$, $a = 7.5080(7)$, $b = 14.723(2)$, $c = 14.8049(15)$ Å, $\beta = 92.957(5)°$, $U = 1634.4(3)$ Å^3, $Z = 4$, $D_c = 1.476$ g cm^{-3}, $F(000) = 768$, μ (Mo$K\alpha$) = 1.442 mm^{-1}.

Atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms are listed in (Table I). Selected bond distances and bond angles are listed in Table II. The Ni(II) atom has octahedral coordination as shown in Figure 1, which is coordinated by three primary amine nitrogens (N(2), N(3) and N(4)), one tertiary nitrogen N(1) and two nitrogens of the thiocyanate ligands (N(5) and N(6)). Nickel lies on an equatorial plane which consists of N(1), N(3), N(5) and N(4) and the axial positions are occupied by N(2) and N(6). The average Ni–N bond distance is 2.12(3) Å, typical for high spin nickel(II) complexes.[1]

TABLE I Atomic coordinates and equivalent isotropic displacement parameters (Å$^2 \times 10^3$). U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

	x/a	y/b	z/c	U_{eq}
Ni1	0.32926(6)	0.73837(3)	0.14703(3)	0.0298(2)
S1	0.79698(17)	0.60217(11)	−0.02836(10)	0.0647(4)
S2	0.5615(2)	0.58283(10)	0.41630(9)	0.0636(4)
N1	0.1382(4)	0.7988(2)	0.2373(2)	0.0343(8)
N2	0.2163(6)	0.7982(3)	0.0273(3)	0.0437(9)
N3	0.1736(6)	0.6216(3)	0.1208(3)	0.0441(9)
N4	0.4974(5)	0.8522(3)	0.1630(3)	0.0438(9)
N5	0.5185(5)	0.6816(3)	0.0616(3)	0.0497(10)
N6	0.4549(5)	0.6736(3)	0.2574(3)	0.0450(9)
C1	0.0067(7)	0.8632(4)	0.1937(4)	0.0559(14)
C2	−0.0478(11)	0.8577(8)	0.0942(7)	0.052(2)
C2′	0.034(2)	0.9073(9)	0.1156(11)	0.041(3)
C3	0.0813(10)	0.8700(5)	0.0263(4)	0.0679(17)
C4	0.0413(7)	0.7248(4)	0.2858(4)	0.0523(12)
C5	−0.0515(8)	0.6517(4)	0.2315(4)	0.0577(14)
C6	0.0694(7)	0.5823(3)	0.1924(4)	0.0528(13)
C7	0.2343(7)	0.8480(3)	0.3139(3)	0.0440(11)
C8	0.3620(7)	0.9233(4)	0.2910(4)	0.0504(12)
C9	0.5335(7)	0.8923(4)	0.2521(4)	0.0512(13)
C10	0.6332(6)	0.6490(3)	0.0240(3)	0.0397(10)
C11	0.5006(6)	0.6364(3)	0.3226(3)	0.0382(10)

TABLE II Selected bond distance (Å) and angles (°)

Ni(1)–N(6)	2.076(4)	Ni(1)–N(2)	2.114(3)
Ni(1)–N(3)	2.100(3)	Ni(1)–N(4)	2.098(3)
Ni(1)–N(5)	2.122(4)	Ni(1)–N(1)	2.199(3)
Ni(2)–Ni(1)–N(4)	89.0(3)	Ni(6)–Ni(1)–N(4)	91.4(4)
N(4)–Ni(1)–N(3)	174.64(14)	N(5)–Ni(1)–N(2)	178.80(14)
N(1)–Ni(1)–N(4)	91.20(13)	N(1)–Ni(1)–N(3)	94.04(13)
N(3)–Ni(1)–N(5)	87.0(2)	N(4)–Ni(1)–N(5)	87.8(2)
N(6)–Ni(1)–N(2)	175.07(4)		

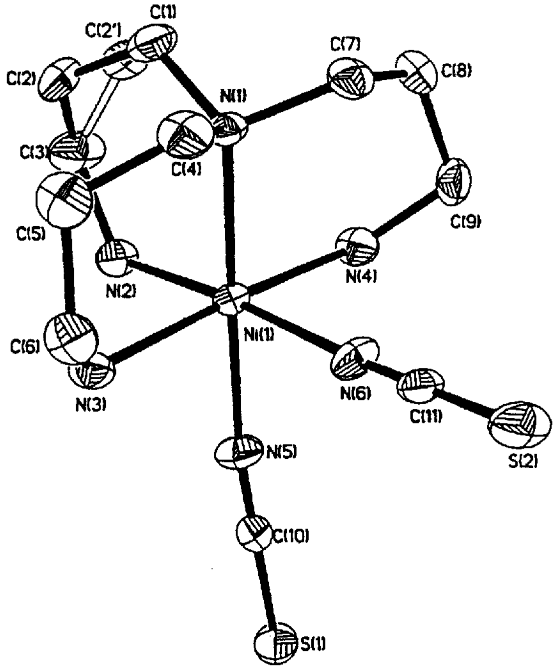

FIGURE 1 Crystal structure of the complex [Ni(trpn)(NCS)$_2$] showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

The sulfur atoms of thiocyanate anions are hydrogen bonded to adjacent primary amine nitrogen atoms. Typical hydrogen bond distances and angles are listed in Table III. The hydrogen bond distance is close to that reported by Serna.[8] Meanwhile, the S2 ··· S2 [$1-x$, $1-y$, $1-z$] distance is 3.631(4) Å, close to the sum of van der Waals radii (3.6 Å) of two sulfur atoms. Thus the complex forms a three-dimensional network of monomers linked through weak intermolecular $S_{NCS}\cdots H{-}N_{amine}$ hydrogen bonds and S ··· S interactions.

TABLE III Typical hydrogen bond distances (Å) and angles (°) (D = donor, A = acceptor)

Donor–H	*d(D–H)*	*d(H···A)*	*∠DHA*	*d(H···A)*	*A*
N(2)–H(2A)	0.803	2.853	154.52	3.595	S2 $[x, -y+3/2, z-1/2]$
N(3)–H(3A)	0.894	2.685	153.58	3.509	S1 $[x-1, y, z]$
N(4)–H(4B)	0.926	2.772	151.56	3.613	S2 $[-x+1, y+1/2, -z+1/2]$

Electrospray Mass Spectrum

The technique of ES-MS sometimes allows pre-existing ions in solution to be transferred very gently into the gas phase with minimal fragmentation.[9] In the positive ion ES-MS of a solution of the complex in methanol, several peak cluster are observed due to five and two isotopes for nickel and carbon atoms, respectively. The mass spectrum is dominated by the peak at m/z 304.1 which is due to $[\mathrm{Ni^{II}(trpn)(NCS)}]^+$. The peak at m/z 246.1 is assigned to $[\mathrm{Ni^{I}(trpn)}]^+$ containing reduced nickel $\mathrm{Ni^I}$. Reduction of the central metal during the ionization process is also found in cobalt(III) cage complexes.[10] The peaks at m/z 666.1 and 1030.1 are due to the formation of new complex ions $[\mathrm{Ni^{II}(trpn)(NCS)_2 + Ni^{II}(trpn)(NCS)}]^+$ and $[\mathrm{Ni^{II}(trpn)(NCS)_2 + Ni^{II}(trpn)(NCS)_2 + Ni^{II}(trpn)(NCS)}]^+$, respectively, in the gas phase. This suggests that the kinds of intermolecular interactions observed in the solid state are significant, and may even persist in solution.

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