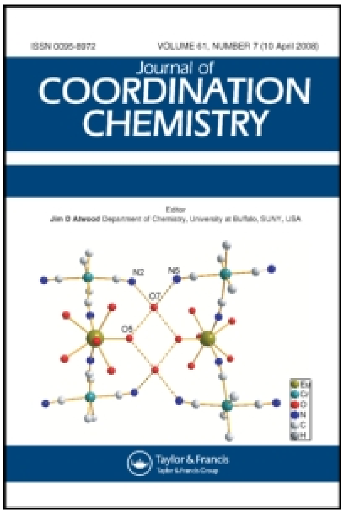

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Synthesis and Characterization of Cu(II), Co(II) and Ni(II) Complexes of Trithiocyanuric Acid: The Structure of {*N,N'*-Bis(3-Aminopropyl)-1,3-Propanediamine}-(Trithiocyanurato)Nickel(II)

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SYNTHESIS AND CHARACTERIZATION OF Cu(II), Co(II) AND Ni(II) COMPLEXES OF TRITHIOCYANURIC ACID: THE STRUCTURE OF {*N*,*N*′-BIS(3-AMINOPROPYL)-1,3-PROPANE-DIAMINE}-(TRITHIOCYANURATO)NICKEL(II)

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Copper, cobalt and nickel complexes with nitrogen donor ligands and trithiocyanurate dianion ($ttcH^{2-}$) have been prepared and characterized by elemental analysis, electronic and EPR (copper complexes) spectra, and magnetic susceptibility measurements over the temperature range 78–291 K. Some of the complexes have also been studied by thermal analysis and by cycle voltammetry. Structures of the complexes have been proposed on the basis of magnetic and spectral properties. Two copper complexes of compositions Cu(bpy)(ttcH) and Cu(phen)(ttcH), where bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, are probably polymeric, whereas the copper complex with *N*,*N*′-bis(3-aminopropyl)ethylenediamine (bapen) of composition [Cu(bapen)ttcH)] · $2H_2O$ is mononuclear. We assume distorted octahedral structures for nickel complexes. A single crystal X-ray analysis of [Ni(bappn)(ttcH)] · $5H_2O$ shows that the central nickel atom is coordinated by tetradentate nitrogen ligand *N*,*N*′-bis(3-aminopropyl)-1,3-propanediamine and coordination is completed by sulfur and nitrogen atoms of trithiocyanurate dianion.

Keywords: Copper(II), cobalt(II) and nickel(II) complexes; Trithiocyanuric acid; Magnetochemical properties; X-ray structure

INTRODUCTION

Coordination chemistry of heterocyclic ligands provides an interesting area since heterocycles play a very important role in life [1]. Trithiocyanuric acid ($ttcH_3$) was,

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for example, used for spectrophotometric determination of copper(II), in a zinc electroplating bath, as a component in PVC floor coverings, and as a preventing agent in vulcanization inhibition [2,3]. The trisodium salt of the acid was used instead of thiourea in single bath full bleaching of wool [4]. From the biochemical point of view, $ttcH_3$ was evaluated as a ligand of toxoplasma gondii uracil phosphoribosyltransferase. The acid is able to inhibit this enzyme *in vitro* better than 5-fluorouracil and emimycin, which have antitoxoplasmal activity [5]. Complexes of Co, Cu and Cd with trithiocyanuric acid in different stoichiometries in controlled pH aqueous solutions have been prepared by Bailey *et al.* The complexes can be used as precursors to transition metal sulfide nanomaterials [6]. In addition to polynuclear species of unknown structures bridged by trithiocyanurate, interesting structures of binuclear and polynuclear complexes have been determined. For example, binuclear complex $[\{Co(en)_2\}_2(ttc)](ClO_4)_3 \cdot 2H_2O$ (en = ethylenediamine) was prepared by Yamanari *et al.* [7] and $[\{Os_3H(CO)_{10}\}_3(ttc)]$ was studied by Ainscough *et al.* [8]. Some structures of main group metals (Ca, Sr and Ba) with trithiocyanuric acid were also reported [9].

In this article, we report our results on Cu(II), Co(II) and Ni(II) complexes with the coordination sphere formed by nitrogen donor ligands and coordinated trithiocyanurate (2−). We investigated the role of the central ion for coordination of $ttcH^{2-}$ and the possibility of polynuclear species formation. We have used magnetochemical measurement at variable temperature for study of the complexes. We prepared single crystals of $[Ni(bappn)(ttcH)] \cdot 5H_2O$, where bappn = *N*,*N*′-bis(3-aminopropyl)-1,3-propanediamine. Although crystals of $[Cu(bapen)(ttcH)] \cdot 2H_2O$ have also been obtained, they were not of sufficient quality for X-ray study.

EXPERIMENTAL

Syntheses

Preparation of $[Cu(bapen)(ttcH)] \cdot 2H_2O$ *(1)*

0.18 mL (1 mmol) of *N*,*N*′-bis(3-aminopropyl)ethylenediamine (bapen) was added to a solution of 0.17 g (1 mmol) of $CuCl_2 \cdot 2H_2O$ in water. Then, 0.4 g (1 mmol) of $ttcNa_3 \cdot 9H_2O$ in water was added with stirring. A small amount of green precipitate was removed by filtration. After a week violet crystals were filtered off, washed with water and dried in the air.

Yield 48%. Anal. Calcd. for $C_{11}H_{27}N_7CuO_2S_3$ (%): C, 29.4; H, 6.1; N, 21.8; S, 21.4. Found: C, 29.1; H, 5.9; N, 21.0; S, 21.9.

Preparation of Cu(bpy)(ttcH) (2)

$Cu(bpy)_2Cl_2 \cdot 4H_2O$ (0.52 g, 1 mmol) was dissolved in water. A solution of $ttcNa_3 \cdot 9H_2O$ (0.4 g, 1 mmol) in water with 1 mL 0.1 M HCl was added. A light green precipitate immediately formed, filtered off, washed with water and ethanol and dried in a desiccator over KOH.

Yield 38%. Anal. Calcd. for $C_{13}H_9N_5CuS_3$ (%): C, 39.5; H, 2.3; N, 17.7; S, 24.4. Found: C, 39.2; H, 2.1; N, 17.6; S, 23.3.

Preparation of Cu(phen)(ttcH) (3)

To a solution of $Cu(CH_3CO_2)_2 \cdot 4H_2O$ (0.2 g, 1 mmol) in water, an ethanol solution of phen (0.4 g, 2.23 mmol) was added 0.4 g (1 mmol) of $ttcNa_3 \cdot 9H_2O$ in water was added with stirring. Light brown precipitate was filtered off, washed with ethanol and dried in a desiccator over KOH.

Yield 46%. Anal. Calcd. for $C_{15}H_9N_5CuS_3$ (%): C, 43.0; H, 2.2; N, 16.7; S, 23.0. Found: C, 43.7; H, 2.2; N, 16.4; S, 22.4

Preparation of [Co(phen)$_2$(ttcH)] · H$_2$O (4)

To a solution of $Co(CH_3CO_2)_2 \cdot 4H_2O$ (0.25 g, 1 mmol) in water, phen (0.4 g, 2.23 mmol) dissolved in ethanol was added, then 0.4 g (1 mmol) of $ttcNa_3 \cdot 9H_2O$ in water was added with stirring. An orange precipitate formed, was filtered on a frit, washed with ethanol and dried under an IR lamp.

Yield 62%. Anal. Calcd. for $C_{27}H_{19}N_7CoOS_3$ (%): C, 52.9; H, 3.1; N, 16.0; S, 15.7; Co, 9.6. Found C, 52.0; H, 3.1; N, 15.7; S, 16.1; Co, 10.1.

Preparation of [Co(taa)(ttcH)] · H$_2$O (5)

0.15 mL (1 mmol) of tris(2-aminoethyl)amine (taa) was added to a solution of 0.24 g (1 mmol) of $CoCl_2 \cdot 6H_2O$ in water. A solution of $ttcNa_3 \cdot 9H_2O$ (1 mmol) in H_2O (10 mL) with 1 mL 0.1 M HCl was then added dropwise. The color of the solution was brown-red and further addition led to formation of brown-red precipitate. Product was filtered off, washed with water and dried under an IR lamp.

Yield 68%. Anal. Calcd. for $C_9H_{21}N_7CoOS_3$ (%): C, 27.1; H, 5.3; N, 24.6; S, 24.1; Co, 14.8. Found: C, 27.4; H, 4.7; N, 24.1; S, 24.3; Co, 15.2.

Preparation of [Co(teta)(ttcH)] · 2H$_2$O (6)

0.2 mL (1.42 mmol) of triethylenetetraamine (teta) was added to a solution of 0.25 g (1 mmol) $Co(CH_3CO_2)_2 \cdot 4H_2O$ in water. With stirring, 0.4 g (1 mmol) of $ttcNa_3 \cdot 9H_2O$ in water was added. The color of the solution turned red and a pink-red precipitate obtained was filtered off, washed with water and dried under an IR lamp.

Yield 74%. Anal. Calcd. for $C_9H_{23}N_7CoO_2S_3$ (%): C, 26.0; H, 5.6; N, 23.5; S, 23.1; Co, 14.2. Found. C, 25.6; H, 4.9; N, 23.1; S, 22.4; Co, 14.2.

Preparation of [Ni(bapenglyoxal)(ttcH)] · 2H$_2$O (7)

$NiCl_2 \cdot 6H_2O$ (0.24 g, 1 mmol) was dissolved in a minimum amount of water. To the solution 0.18 mL (1 mmol) of *N*,*N*′-bis(3-aminopropyl)ethylenediamine and 0.07 g (0.33 mmol) of trimeric glyoxal dihydrate were added with stirring. The reaction mixture was boiled under reflux for one hour. After cooling, 0.4 g (1 mmol) of $ttcNa_3 \cdot 9H_2O$ with 1 mL of 0.1 M HCl in water was added. The brown solution was left standing overnight to obtain brown precipitate which was filtered on a frit, washed with water and ethanol and dried under an IR lamp.

Yield 55%. Anal. Calcd. for $C_{13}H_{25}N_7NiO_2S_3$ (%): C, 33.5; H, 5.4; N, 21.0; S, 20.6; Ni, 12.6. Found: C, 33.9; H, 5.2; N, 20.6; S, 20.4; Ni, 12.6.

Preparation of [Ni(bpy)$_2$(ttcH)] · 2H$_2$O (8)

$Ni(CH_3CO_2)_2 \cdot 4H_2O$ (0.25 g, 1 mmol) was dissolved in ethanol and 0.32 g (2.04 mmol) of bpy in ethanol was added. The solution was boiled and after cooling, 0.4 g (1 mmol) of $ttcNa_3 \cdot 9H_2O$ in water was added dropwise. During addition formation of light green precipitate was observed. Product was filtered off, washed with ethanol and dried under an IR lamp.

Yield 42%. Anal. Calcd. for $C_{23}H_{21}N_7NiO_2S_3$ (%): C, 47.4; H, 3.6; N, 16.8; S, 16.5; Ni, 10.1. Found: C, 47.9; H, 3.2; N, 16.4; S, 15.8; Ni, 10.7.

Preparation of [Ni(dpa)$_2$(ttcH)] · H$_2$O (9)

The complex was prepared similarly to that above with 0.4 g (2 mmol) of 2,2′-dipyridylamine (dpa) used instead of bpy.

Yield 46%. Anal. Calcd. for $C_{23}H_{21}N_9NiOS_3$ (%): C, 46.5; H, 3.6; N, 21.2; S, 16.2; Ni, 9.9. Found: C, 46.4; H, 3.5; N, 20.6; S, 15.2; Ni, 10.8.

Preparation of [Ni(bappn)(ttcH)] · 5H$_2$O (10)

0.2 mL (1 mmol) of *N*,*N*′-bis(3-aminopropyl)-1,3-propanediamine (bappn) was added to a solution of $Ni(CH_3CO_2)_2 \cdot 4H_2O$ (0.25 g, 1 mmol) in water. Finally, $ttcNa_3 \cdot 9H_2O$ (0.4 g, 1 mmol) in water was added with stirring. Blue-green crystals were obtained by slow evaporation after a week, washed with a minimum of water and dried in the air. These crystals were used for X-ray analysis.

Yield 62%. Anal. Calcd. for $C_{12}H_{28}N_7NiO_{1,5}S_3$ (%): C, 32.1; H, 6.3; N, 21.8; S, 21.4. Found. C, 32.9; H, 6.0; N, 21.3; S, 19.9.

Physical Measurements

C, H, N, S analyses were carried out on an EA 1108 instrument (Fisons). Diffuse-reflectance spectra were recorded on a Specord M 40 (Carl Zeiss, Jena), using Nujol mulls in the 40 000–11 000 cm^{-1} region. EPR measurements were performed at 90 K as frozen dimethylformamide solutions with an ESR 221 (ZWG Berlin) spectrometer. Temperature dependence of magnetic susceptibility was measured by the Faraday method in the range 78–291 K. $Hg[Co(SCN)_4]$ was used as a calibrant. The correction for diamagnetism was calculated using Pascal's constants. Thermal decomposition was studied with an Exstar 6000 (Seiko Instruments Inc.) with a sample weight of 5–10 mg and rate of temperature increase of 2.5°C min^{-1}. The electrochemical properties of the prepared complexes were investigated in propylene carbonate (PC) solution using cyclic voltammetry, and in the solid state by the method of abrasive voltammetry. Experiments were carried out using a computerized electrochemical measuring system Eco-Tribo Polarograf (Polaro-Sensors s.r.o., Prague, Czech Republic) with a three-electrode cell arrangement (a Pt sheet as auxillary electrode). The Pt disc working electrode (0.5 mm diameter, 0.00196 cm^2), and nonaqueous ferrocene/ferrocenium reference electrode (E^0 of the ferrocene/ferrocenium couple was +280 mV, $\Delta E_p = 70$ mV), were used for measurements in a PC solution. Tetraethylammonium perchlorate (TEAP) (concentration 0.1 M) was used as a supporting electrolyte. The glassy carbon working electrode and the aqueous saturated

TABLE I Crystal data and structure refinement for [Ni(bappn)(ttcH)] · 1.5H$_2$O

Empirical formula	$C_{24}H_{58}N_{14}Ni_2O_3S_6$
Formula weight	900.62
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions	$a = 15.359(3)$ Å $b = 16.265(3)$ Å $c = 31.048(6)$ Å
Volume	7756(3) Å^3
Z	8
Absorption coefficient	1.343 mm^{-1}
F(000)	3808
Density (cald.)	1.543 Mg m^{-3}
Crystal size	0.60 × 0.25 × 0.25 mm
Index ranges	$-18 \leq h \leq 18$, $-19 \leq k \leq 11$, $-36 \leq l \leq 33$
Reflections collected	32385
Independent reflections	6770 [R(int) = 0.0475]
Refinement method	Full-matrix least-squares on F^2
Data–restraints–parameters	6770–0–605
Goodness-of-fit on F^2	1.023
Final R indices [$I > 2\sigma(I)$]	$R = 0.0592$, $R_w = 0.1496$
R indices (all data)	$R = 0.0698$, $R_w = 0.1549$

calomel reference electrode (SCE) were used in the case of the abrasive voltammetry measurements. Potassium chloride aqueous solution (0.1 M) was used as supporting electrolyte. Scan rate varied from 0.01 to 20 V s^{-1}.

Crystal Structure Determination

Crystals of [Ni(bappn)(ttcH)] · 1.5H$_2$O were obtained by slow evaporation of a water solution of the complex. The crystallographic data are listed in Table I and final fractional atomic coordinates for the nonhydrogen atoms are listed in Table II.

X-ray data were collected on a four-circle κ-axis KUMA KM-4 diffractometer equipped with an Oxford Cryostream cooler using graphite-monochromated MoK$_\alpha$ radiation. Data collections were perfomed using a CCD detector (KUMA Diffraction, Wroclaw). KUMA KM4RED software was used for data reduction. The structures were solved using direct methods (SHELXS-97) [10] and refined on F^2 using full-matrix least-squares procedure (SHELXL-97) [11] with weight: $w = 1/[\sigma^2(F_0^2) + (0.0676P)^2 + 52.5425P]$, where $P = (F_0^2 + 2F_c^2)/3$. All hydrogen atoms were located in difference Fourier maps. The largest peak and hole on the final difference map were 2.02 e · Å^{-3} [1.17 Å from S(4)] and -1.37 e · Å^{-3} [0.74 Å from Ni(2)].

RESULTS AND DISCUSSION

For the syntheses of copper complexes we have used a tetradentate aliphatic *N*-donor ligand (bapen) and bidentate aromatic heterocycles (bpy, phen).

On the basis of thermal analysis of the complex [Cu(bapen)(ttcH)] · 2H$_2$O (1) we assume that water molecules are not coordinated. This complex starts to decompose at 50°C accompanied by a loss of two molecules of water ($\Delta m = 7.6\%$, calcd. 8.0%) and

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for [Ni(bappn)(ttch)] · 1.5H_2O. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Ni(1)	1996(1)	968(1)	5254(1)	16(1)
Ni(2)	7115(1)	1434(1)	7109(1)	29(1)
S(1)	1309(1)	−263(1)	4880(1)	20(1)
S(2)	−905(1)	959(1)	3729(1)	24(1)
S(3)	999(1)	2926(1)	4682(1)	22(1)
S(4)	7850(1)	222(1)	7465(1)	35(1)
S(5)	9504(1)	1428(1)	8830(1)	19(1)
S(6)	7932(1)	3390(1)	7731(1)	37(1)
N(1)	2643(3)	337(3)	5739(2)	24(1)
C(2)	3178(4)	−384(3)	5621(2)	30(1)
C(3)	3877(4)	−180(3)	5296(2)	32(1)
C(4)	3536(4)	4(3)	4846(2)	29(1)
N(5)	3093(3)	817(2)	4820(2)	22(1)
C(6)	3754(4)	1469(3)	4764(2)	31(1)
C(7)	3391(4)	2327(3)	4831(2)	26(1)
C(8)	3185(3)	2505(3)	5298(2)	22(1)
N(9)	2331(3)	2181(3)	5439(1)	18(1)
C(10)	2189(3)	2389(3)	5897(2)	23(1)
C(11)	1249(4)	2342(3)	6038(2)	28(1)
C(12)	883(4)	1476(3)	6059(2)	28(1)
N(13)	854(3)	1101(3)	5630(2)	21(1)
N(14)	1164(3)	1288(2)	4716(1)	18(1)
C(15)	865(3)	528(3)	4594(2)	18(1)
N(16)	272(3)	390(2)	4287(1)	20(1)
C(17)	−104(3)	1046(3)	4106(2)	17(1)
N(18)	151(3)	1809(3)	4236(1)	17(1)
C(19)	776(3)	1951(3)	4539(2)	16(1)
N(21)	6156(4)	1349(5)	7582(2)	61(2)
C(22)	5333(5)	1798(6)	7543(3)	65(2)
C(23)	5481(5)	2673(7)	7439(4)	85(4)
C(24)	5825(5)	2857(5)	6982(3)	63(3)
N(25)	6740(4)	2619(3)	6923(2)	44(1)
C(26)	7019(6)	2831(5)	6471(2)	62(2)
C(27)	7962(6)	2934(5)	6414(3)	68(2)
C(28)	8573(6)	2334(5)	6642(3)	59(2)
N(29)	8192(4)	1503(3)	6670(2)	43(1)
C(30)	8160(5)	1108(5)	6244(2)	55(2)
C(31)	7649(5)	291(5)	6244(2)	53(2)
C(32)	6662(5)	423(5)	6271(2)	58(2)
N(33)	6349(4)	761(3)	6681(2)	41(1)
N(34)	7966(3)	1757(3)	7632(1)	24(1)
C(35)	8184(3)	1006(3)	7785(2)	25(1)
N(36)	8639(3)	863(2)	8152(1)	24(1)
C(37)	8891(3)	1514(3)	8376(1)	16(1)
N(38)	8661(3)	2283(2)	8235(1)	20(1)
C(39)	8190(3)	2418(3)	7864(2)	23(1)
O(1)	5431(4)	−380(4)	7341(2)	84(2)
O(2)	9046(5)	−825(3)	8241(2)	81(2)
O(3)	4727(5)	324(4)	8153(3)	107(3)

an *endo*-effect occurs on the DTA curve. An anhydrous form of the complex (1) is thermally stable between 120 and 180°C. Consequently, the complex decomposes slowly and a plateau is observed from 370 to 480°C. Decomposition is finished near 800°C and the final product of decomposition was determined by powder diffraction as CuO.

The complex (1) has an effective magnetic moment (see Table III) equal to 1.78 BM, which is typical of one unpaired electron systems, and the value is consistent

TABLE III Magnetic and spectral data for the complexes

Compound	μ_{eff}/BM 294 K	μ_{eff}/BM 78 K	$\lambda_{\max} \times 10^3$ (cm^{-1})
(1) [Cu(bapen)(ttcH)] · $2H_2O$	1.80	1.78	18.0, 28.2
(2) Cu(bpy)(ttcH)	1.28	1.22	14.0, 29.0
(3) Cu(phen)(ttcH)	1.23	1.17	14.0, 29.0
(4) [Co(phen)$_2$(ttcH)] · H_2O	4.14	–	29.8, 34.0
(5) [Co(taa)(ttcH)] · H_2O	1.29	1.18	20.0, 28.8
(6) [Co(teta)(ttcH)] · $2H_2O$	0.63	0.36	19.4, 32.0
(7) [Ni(bapenglyoxal)(ttcH)] · $2H_2O$	2.46	–	15.0, 29.0
(8) [Ni(bpy)$_2$(ttcH)] · $2H_2O$	3.39	–	16.8, 29.8, 32.6
(9) [Ni(dpa)$_2$(ttch)] · H_2O	3.27	–	29.1, 37.6
(10) [Ni(bappn)(ttcH)] · $1.5H_2O$	3.06	–	16.6, 28.4, 34.5

with previous observations of similar complexes [12]. The magnetic moment of the complex changes little with temperature decrease and the data were fitted to the Curie–Weiss law with $C = 0.405(1)\,\mathrm{cm^3\,mol^{-1}\,K^{-1}}$ and $\Theta = -3.5(4)$ K. Two bands are observed in the electronic spectrum of (1); the band at 28 200 cm^{-1} is due to a π–π^* transition located on ttcH^{2-} and that at 18 000 cm^{-1} can be associated with a *d*–*d* transition [13].

The room temperature values of μ_{eff} of 1.28 and 1.23 BM calculated for Cu(bpy)(ttcH) (2) and Cu(phen)(ttcH) (3), respectively, are very low for Cu(II) with one unpaired electron (spin only value is equal to 1.73 BM). The magnetic moments show only small temperature dependence and the susceptibility data were fitted to the Curie–Weiss expression affording $C = 0.2058(6)\,\mathrm{cm^3\,mol^{-1}\,K^{-1}}$ and $\Theta = -9.1(5)$ K for (2), and $C = 0.1932(7)\,\mathrm{cm^3\,mol^{-1}\,K^{-1}}$ and $\Theta = -10.3(6)$ K for (3), respectively. The low values of μ_{eff} at room temperature and the negative values of the Weiss constant may indicate presence of an antiferromagnetic interaction in both these complexes. This interaction, if present, could only be detected unambiguously by measurements of susceptibility data to lower temperatures. We also tried to interpret susceptibility data by using other mathematical models both for binuclear and polymeric copper(II) compounds. Unfortunately, our attempts to find concordance between experimental and theoretical data were unsuccessful. The reflectance spectra of (2) and (3) involve a broad band centered at 14 000 cm^{-1} due to a *d*–*d* transition, however, no detailed conclusions regarding the geometry can be made. The EPR spectra of (1) and (3) are very similar to each other. They are of rhombic type with $g_1 = 2.21$, $g_2 = 2.06$, $g_3 = 1.98$ and $g_1 = 2.21$, $g_2 = 2.07$, $g_3 = 1.98$, respectively. There is only one resolved hyperfine splitting parameter of 196 Gauss in both spectra. The complex (2) shows an axial EPR spectrum with $g_1 = 2.26$, $g_2 = 2.04$ and $A_1 = 165$ Gauss. The reflectance and EPR spectra indicate structures with a local spin $S = 1/2$ [14].

The coordination sphere of three cobalt complexes (4)–(6) is formed by trithiocyanurate ion and is completed by two phenanthrolines (4) or by tetradentate amines (5) and (6). The effective magnetic moment for (4) is in the range expected for octahedral Co(II) high-spin complexes with only a small orbital contribution (the spin only value for three unpaired electrons is 3.89 BM). Bis-phenanthroline cobalt(II) complexes with various coordinated anions have μ_{eff} values in the 4.7–5.2 BM range [15]. In the diffuse-reflectance spectrum of (4) only bands attributable to π–π^* or CT transitions were observed. Other than these bands, there is one more band in the spectra of complexes (5) and (6) with a maximum about 20 000 cm^{-1}, which can be due to *d*–*d* transition. Magnetic moments of (5) and (6) at room temperature are lower than the expected for low spin Co(II) complexes with one unpaired electron. Magnetic moments of both these complexes slightly decrease with decrease of temperature. The data for (5) were fitted to the Curie–Weiss law affording $C = 0.214(1)\,\mathrm{cm^3\,mol^{-1}\,K^{-1}}$ and $\Theta = -20.6(8)\,\mathrm{K}$. The negative value of the Weiss constant shows a possibility of antiferromagnetic interaction among paramagnetic centers. We also cannot exclude partial oxidation of cobalt ions, especially in complex (6), and its composition may be better formulated as [Co(teta)(ttc)] $\cdot$ $2H_2O$, where the acid is completely deprotonated. We conclude from thermal analysis that there is no coordinated water molecule in (6). Thermal decomposition of (6) begins at 50°C with loss of two water molecules ($\Delta m = 8.7\%$, calcd. 8.7%). This process is accompanied by an *endo*-effect seen on the DTA curve. A plateau, appearing on the TGA curve in the range of 110–200°C, corresponds to existence of an anhydrous complex. Further decomposition of this complex is accompanied with an *exo*-effect. Final product of decomposition is Co_3O_4 as confirmed by powder diffraction data.

Three new nickel(II) complexes have been prepared. We have used bidentate *N*-donor ligands bpy and dpa, and a macrocyclic ligand 1,4,8,11-tetraazacyclotetradeca-1,3-diene, formed by template condensation of *N*,*N′*-bis(3-aminopropyl)ethylenediamine and glyoxal, as a tetradentate *N*-donor. As can be seen from Table III, the μ_{eff} value calculated for (7) is somewhat lower than a spin only value (2.83 BM) for two unpaired electrons. From the μ_{eff} value (2.46 BM) we assume that coordination of both bapenglyoxal and trithiocyanurate dianion occurs. The lower value of magnetic moment arises from an interaction among paramagnetic nickel(II) centers or by formation of a polynuclear complex. Magnetic moments of complexes (8) and (9) are typical of octahedral nickel(II) complexes [12]. All the nickel complexes are insoluble in usual solvents including DMF and we were not able to obtain solution spectra. Maxima observed in diffuse-reflectance spectra at 15 000 and 16 800 $\mathrm{cm^{-1}}$, for (7) and (9), respectively, (see Table III) can be assigned to *d–d* transitions. Owing to the *pseudo*-octahedral geometry of the complexes we did not assign the transition. The bands with maxima found at 29 000–29 800 $\mathrm{cm^{-1}}$, where other *d–d* transitions should be expected, are overlapped with a π–π^* transition located on $\mathrm{ttcH^{2-}}$ or imines [13]. The bands in the UV region can be assigned to CT transitions.

Coordination of $\mathrm{ttcH^{2-}}$ and four *N*-donor atoms in distorted octahedral geometry is demonstrated for complex (10). This complex was prepared previously and characterized [16]. Here we present a similar preparation method, leading to formation of crystalline material, and results of an X-ray study.

The structure of [Ni(bappn)(ttcH)] $\cdot$ $1.5H_2O$ (10) consists of two crystallographically independent molecules. A view of the molecules is shown in Fig. 1, while selected bond lengths and angles are listed in Table IV. The coordination polyhedron around the nickel atom is a distorted octahedron with a NiN_5S chromophore. Nickel is coordinated by four nitrogen atoms of bappn and by *S*- and *N*-donor atoms of $\mathrm{ttcH^{2-}}$. The Ni(1)–N bond lengths of the first molecule are in the range of 2.075(5) to 2.171(4) Å and the Ni(1)–S(1) distance is 2.5448(13). The Ni(2)–N bond lengths in the second molecule lie in 2.084(6)–2.149(4) Å range, while Ni(2)-S(4) is equal to 2.5249(16) Å. When we compare structure of (10) with that of [Ni(bapen)(ttcH)] $\cdot$ $2H_2O$ (bapen = *N*,*N′*-bis(3-aminopropyl)ethylenediamine) [16] we can see that the bond lengths and angles around nickel (Ni–N are in the 2.077 (4)–2.143(3) Å range, Ni–S bond distance is 2.5208(16) Å are better comparable with the values found for the second molecule in (10).

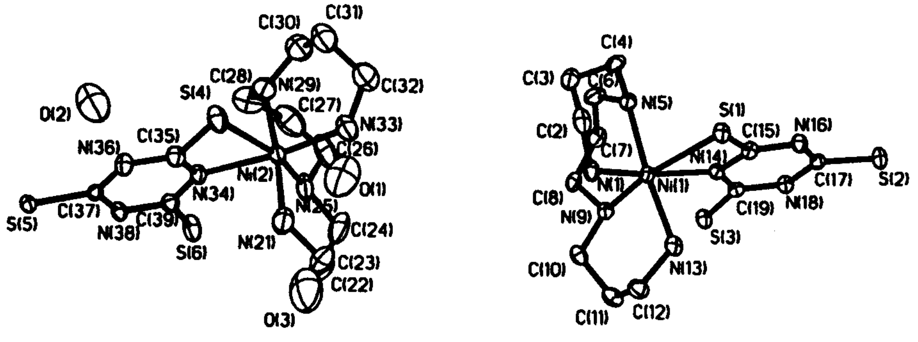

FIGURE 1 Molecular structure of [Ni(bappn)(ttcH)] · $1.5H_2O$. H atoms were omitted for clarity.

TABLE IV Selected bond lengths [Å] and angles [°] for [Ni(bappn)(ttcH)] · $1.5H_2O$

Ni(1)–N(1)	2.075(5)	Ni(2)–N(21)	2.084(6)
Ni(1)–N(9)	2.117(4)	Ni(2)–N(33)	2.085(5)
Ni(1)–N(13)	2.119(5)	Ni(2)–N(25)	2.094(5)
Ni(1)–N(14)	2.168(4)	Ni(2)–N(34)	2.149(4)
Ni(1)–N(5)	2.171(4)	Ni(2)–N(29)	2.146(5)
Ni(1)–S(1)	2.5448(13)	Ni(2)–S(4)	2.5249(16)
N(1)–Ni(1)–N(9)	98.55(19)	N(21)–Ni(2)–N(33)	90.8(2)
N(1)–Ni(1)–N(13)	92.7(2)	N(21)–Ni(2)–N(25)	93.5(3)
N(9)–Ni(1)–N(13)	87.54(17)	N(33)–Ni(2)–N(25)	98.7(2)
N(1)–Ni(1)–N(14)	163.77(18)	N(21)–Ni(2)–N(34)	85.1(2)
N(9)–Ni(1)–N(14)	97.39(16)	N(33)–Ni(2)–N(34)	162.37(19)
N(13)–Ni(1)–N(14)	84.95(17)	N(25)–Ni(2)–N(34)	98.64(19)
N(1)–Ni(1)–N(5)	91.31(19)	N(21)–Ni(2)–N(29)	174.6(2)
N(9)–Ni(1)–N(5)	94.93(16)	N(33)–Ni(2)–N(29)	93.3(2)
N(13)–Ni(1)–N(5)	174.91(18)	N(25)–Ni(2)–N(29)	89.3(2)
N(14)–Ni(1)–N(5)	90.31(16)	N(34)–Ni(2)–N(29)	89.92(19)
N(1)–Ni(1)–S(1)	98.04(15)	N(21)–Ni(2)–S(4)	87.53(19)
N(9)–Ni(1)–S(1)	163.24(13)	N(33)–Ni(2)–S(4)	96.98(15)
N(13)–Ni(1)–S(1)	89.31(13)	N(25)–Ni(2)–S(4)	164.25(16)
N(14)–Ni(1)–S(1)	65.92(10)	N(34)–Ni(2)–S(4)	65.76(11)
N(5)–Ni(1)–S(1)	87.05(12)	N(29)–Ni(2)–S(4)	88.53(15)

Electrochemical studies of the complexes (1), (4), (5) and (6) in the potential range -700 to $+1300$ mV revealed some interesting results only in the case of (4). There is a clearly visible redox pair of Co^{2+}/Co^{3+} at the potential $E^{o,} = 230$ mV on the cyclic voltammogram of this complex (see Fig. 2). As the redox process is nearly reversible by the values of the $\Delta E_p = 70$ mV and $I_p^a/I_p^c = 1$, the values of the peak currents $I_p = 33$ nA are only 1/10 of the values for ferrocene/ferrocenium redox pair. The second oxidation peak at the potential about 650 mV can be attributed to the irreversible oxidation of $ttcH_3$. The electrochemical behavior of (4) in the solid state (abrasive voltammetry) is very close to the results obtained in PC solution (see Fig. 3). The cyclic voltammograms of (1) and (6) contain only one irreversible anodic peak about 675 mV which can be attributed to the oxidation of $ttcH_3$. Abrasive voltammetric measurement of (1), (5) and (6) supports this result because there is only broad oxidation peak above 400 mV on voltammograms. The peak of the same maximum was also observed in $ttcH_3$ voltammogram [17].

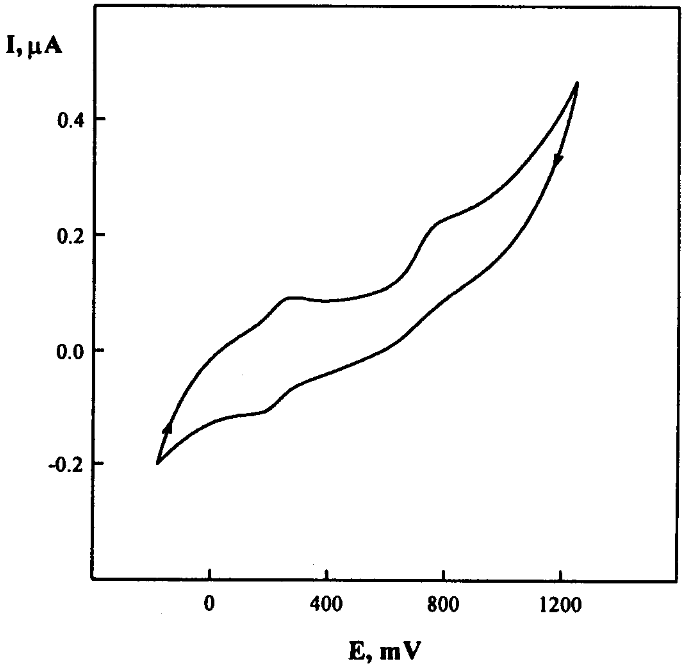

FIGURE 2 Cyclic voltammogram of (4) in PC solution ($c = 10^{-3}\,\mathrm{mol\,L^{-1}}$) on Pt disc electrode taken at scan rate of $50\,\mathrm{mV\,s^{-1}}$.

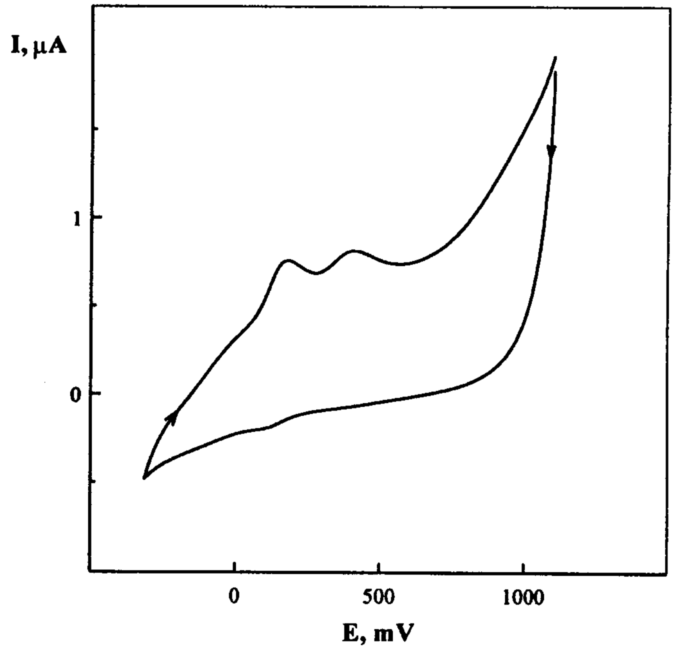

FIGURE 3 Cyclic voltammogram of the solid (4) on gC disc electrode taken at scan rate of $50\,\mathrm{mV\,s^{-1}}$.

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Supplementary Data

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 166847. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk) or also available from the author Zdeněk Trávníček.

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