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Mononuclear complexes of 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole containing tripodal tris(3-aminopropyl)amine: crystal structure of [Ni(trpn)(abpt)](ClO_4)$_2$

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Abstract

Complexes of the type [M(trpn)(abpt)](ClO_4)$_2$ (**1**–**6**) [M = Mn, Fe, Co, Ni, Cu, Zn, trpn = tris (3-aminopropyl)amine, abpt = 4-amino-3,5-bis (pyridin-2-yl)-1,2,4-triazole] have been synthesized. The mode of bonding and overall geometry of these complexes have been deduced by elemental analyses data, molar conductance values, spectral studies obtained from FT-IR, ^{1}H NMR and electronic spectral analyses and magnetic susceptibility measurements. The structure of complex **4** has been determined by single X-ray crystallography. On the basis of the above physicochemical studies and the single X-ray crystallographic data recorded on complex **4**, an octahedral geometry has been suggested for all the complexes.

Keywords: Trpn; Abpt; Monoclinic; Crystal; Octahedral geometry; Intramolecular hydrogen bonding

1. Introduction

The coordination chemistry of the ligand 4-amino-3,5-bis-(pyridin-2-yl)-1,2,4-triazole (abpt) (Fig. 1) was initiated by Reedijk and coworkers. They reported [1–6] a variety of mononuclear and/or dinuclear complexes of transition metals with interesting spectroscopic and X-ray crystallographic studies and established a preferred chelating behaviour involving the nitrogens of the triazole and pyridyl group. However, Rheingold et al. [7] have shown an ambidentate behaviour of this bidentate ligand and reported X-ray crystal structures of two bidentate coordination isomers where the metal is co-ordinated to a pyridyl nitrogen and the amino nitrogen in addition to the usual coordination of metal to a pyridyl and the triazole nitrogen atom.

Reedijk and coworkers [3] have also reported compounds of the types, M(abpt) (TCNQ) and M(abpt)$_2$ (TCNQ)$_2$ [M = Fe, Co, Ni, Cu, TCNQ = 7,7′,8,8′-tetracynoquinodimethanido anion] in an attempt to obtain molecular metals and to investigate their conducting, magnetic and spectroscopic properties similar to the highly conducting compounds Cu(Phen)$_2$(TCNQ)$_2$ or Cu(bpy)$_2$(TCNQ)$_2$ [Phen = 1,10-phenanthroline and bpy = 2,2′-bipyridine] [8,9]. However, these compounds are rare examples with the TCNQ radical anion being involved in coordination, and a unique type of Fe(II) spin cross-over has been noticed at room temperature.

A variety of polypyridyl complexes of Ru(II) have been reported [10–12] in view of their interesting spectroscopic, photophysical, photochemical and electrochemical properties due to their application towards the construction of supramolecular systems and photochemically driven molecular devices [13,14]. The general approach taken in electron transfer studies has been to bind the electron acceptor/donor to the ruthenium polypyridyl centre via the polypyridyl ligands [15,16].

The development of artificial nucleases for their use in molecular genetics and genetic engineering has been a challenging research field due to stability of the phosphate diester backbone and its resistivity to hydrolytic cleavage. Metal complexes [17,18] which are ideally

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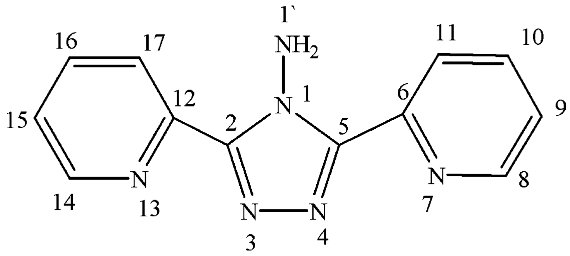


Fig. 1. Structural formula and numbering of 4-amino-3,5-bis-(pyridin-2-yl)-1,2,4-triazole.

catalytic have been proved to be preferred over sequence-specific binding agents [19–21] for hydrolytic cleavage of DNA. Non-redox active metals such as Ni(II), Zn(II) are potentially of interest as hydrolytic cleaving agents and their resistivity in model systems may lead to a functional DNA cleaving molecule.

In view of the fact that $[Ni(tren)]^{2+}$ catalyses the hydrolysis of bis-(4-nitrophenyl)-phosphate at 75 °C in alkaline medium [19], efforts have been directed towards a better understanding of the metal nitrogen bond in complexes derived from azolate bases and a nucleic acid constituent with $[M(tren)]^{2+}$ complexes [22,23].

We therefore thought it worthwhile to synthesize mononuclear complexes of the type [M(trpn)(abpt) $(ClO_4)_2$ (M = Mn, Fe, Co, Ni, Cu, Zn, trpn = tris(3-aminopropyl)amine, abpt = 4-amino-3,5-bis-(pyridin-2-yl)-1,2,4-triazole)] in order to investigate the mode of bonding of abpt in the presence of the tripodal tetra-amine ligand, trpn. The present paper deals with synthesis and physicochemical studies of these complexes and the X-ray crystal structure of [Ni(trpn)(abpt)] $(ClO_4)_2$].

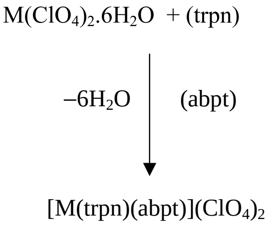
2. Experimental

2.1. Materials and method

The metal salts $M(ClO_4)_2 \cdot 6H_2O$ (all Aldrich) (M = Mn, Fe, Co, Ni, Cu, Zn) were commercially pure samples. The chemicals, tris-(3-aminopropyl)amine (trpn) (TCI, Tokyo Kasei) and 4-amino-3,5-bis-(pyridin-2-yl)-1,2,4-triazole (Aldrich) were used as received. The solvents methanol and methyl cyanide were dried before use.

2.2. Synthesis of ternary metal–trpn–abpt complexes

A methanolic solution (10 ml) of trpn (0.3 mmol) was mixed with a methanolic solution (10 ml) of $M(ClO_4)_2{\cdot}6H_2O$ (0.3 mmol) (M = Mn, Fe, Co, Ni, Cu, Zn) followed by addition of 0.3 mmol solution of abpt dissolved in 10 ml of acetonitrile and water (3:1) at 60 °C. The reaction mixture was magnetically stirred for 4–6 h at room temperature and allowed to stand for 6 days resulting in microcrystalline solids for Mn(II), Fe(II), Co(II), Cu(II), and Zn (II). However good quality single crystals were obtained for Ni(II) (Scheme 1).



M = Mn, Fe, Co, Ni, Cu and Zn
trpn = tris(3-aminopropyl)amine
abpt = 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole

Scheme 1.

The elemental analyses were obtained from the microanalytical laboratory of CDRI, Lucknow, India. The FT-IR spectra (4000–200 cm^{-1}) were recorded as KBr pellets on a Perkin–Elmer 2400 spectrophotometer. The ^1H NMR spectra were recorded on a Jeol Eclipse 400 NMR spectrometer in DMSO-d_6. Metals and chlorides were determined volumetrically [24] and gravimetrically [25], respectively. The electronic spectra of the complexes in DMSO were recorded on a pye-unicam 8800 spectrophotometer at room temperature. Magnetic susceptibility measurements were carried out using a Faraday balance at 25 °C. However, the temperature dependence of magnetic susceptibility for the complex $[Fe(trpn)(abpt)](ClO_4)_2$ was recorded on a quantum design SQUID magnetometer under field cooled conditions between 298 and 4.5 K at 1000G. The electrical conductivities of 10^{-3} M solutions in DMSO were obtained on a digital APX 185 conductivity bridge equilibrated at 25 ± 0.01 °C.

Crystals of complex **4** were obtained from a methanol solution. A bar shaped specimen cut from a bulky crystal was mounted on the tip of a thin glass fiber for X-ray examination and data collection. All data were collected on a Rigaku AFC7R diffractometer with graphite monochromated Mo Kα radiation.

2.3. Crystal data $[Ni(trpn)(abpt)](ClO_4)_2$

Formula weight = 684.19, space group = $P2_1/n$, a (Å) = 8.3835 (3), b (Å) = 20.4591 (2), c (Å) = 16.9702 (2), β (°) = 95.443 (1), V (Å^3) = 2897.60 (7), $Z = 4$, $F(000) = 1424$, $D_{cal} = 1.568$, T (K) = 293, μ(Mo Kα) (cm^{-1}) = 0.917. Scan rate (° min^{-1} in ω) = 16, 2θ range (°) = 3.0 to 55.0, number of reflections measured = 7459, number of unique reflections used ($I_0 > 2\sigma I_c$) (M) = 4014, variables (N) = 415, $S = 1.039$, Max./min. residual (eÅ^{-3}) 0.538/−0.978.

Refinement based on $|F|$, converged at a final R value of 0.073 ($wR_2 = 0.252$) defined by $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $wR_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

3. Results and discussion

A few ternary complexes of first row transition metals, [M(trpn)abpt]$(ClO_4)_2$ have been prepared by the reaction of $M(ClO_4)_2 \cdot 6H_2O$ with trpn and abpt. Complexes **1**–**3**, **5** and **6** are microcrystalline solids whereas the complex **4** gave deep violet coloured crystals suitable for single X-ray crystallography. All the complexes are stable in air for extended periods of time. These are thermally stable up to their melting points and were found to be soluble in DMSO, water, methanol and acetonitrile. The results of elemental analyses (Table 1) suggest that the complexes are formed with the proposed composition as [M(trpn)(abpt)]$(ClO_4)_2$. The molar conductance values (Table 1) measured in DMSO (10^{-3} M) are indicative [26] of 1:2 electrolyte nature of the complexes.

The preliminary identification regarding the nature of bonding of the ligands trpn and abpt have been obtained from the bands obtained in the IR spectra (Table 2). The IR spectra reveal that both trpn and abpt moieties have been coordinated to the metal ion. The coordination of NH_2 groups of trpn may be inferred [23] from a negative shift in both νNH_2 (3185–3295 cm^{-1}) and δNH_2 (1580–1600 cm^{-1}) vibrations. However, lowering of the frequency corresponding to the free NH_2 group of abpt may attributed to intramolecular hydrogen bonding ($N_{13}\cdots N_{1'}$). A sharp band around 410–440 cm^{-1} corresponds [23] to $\nu(M–N)_{trpn}$ vibration. The main spectral variations of the complexes (**1**–**6**) compared to the free abpt ligand are found in the 408–415 cm^{-1} region (out of plane ring deformation) and 604–612 cm^{-1} (in plane ring deformation) [27,28], where absorption of the pyridine ring of abpt ligand occurs. These vibrations are found to be positively shifted suggesting the coordination of the pyridine nitrogen atom (N_7) to the metal atom. However, ring vibrations in the higher frequency region (1575–1590 cm^{-1}) have not been affected appreciably. A negative shift (10–30 cm^{-1}) in the $\nu(C{=}N)$ vibration of the triazole ring suggests [29] coordination via its N_4 atom. In view of the close proximity of absorption bands arising from $\nu(M–N)_{trpn}$ and pyridyl group of abpt in the region 408–415 cm^{-1}, some peaks were difficult to assign. Strong intensity bands appearing in the region 215–235 cm^{-1} may reasonably be assigned to $\nu(M–N_{abpt})$ vibrations which is consistent with bands observed in complexes derived from the ligands with nitrogen donors [30,31]. All the complexes show medium intensity bands in the region 1081–1382 and 930–945 cm^{-1} which may reasonably be assigned [32] to perchlorate (ClO_4^{2-}) vibration modes.

Table 1
% yield, colour, molar conductance and analytical data for the compounds

	Compound	Yield (%)	Colour	Found (Calc.)%					Molar conductivity ($ohm^{-1}\,cm^{-2}\,mol^{-1}$)
				M	Cl	C	H	N	
1	[Mn(trpn)(abpt)]$(ClO_4)_2$	30	Yellow	8.00 (8.07)	10.40 (10.42)	37.00 (37.07)	5.00 (5.03)	20.56 (20.58)	98
2	[Fe(trpn)(abpt)]$(ClO_4)_2$	50	Brown	8.17 (8.19)	10.39 (10.40)	37.00 (37.02)	5.00 (5.02)	20.53 (20.55)	110
3	[Co(trpn)(abpt)]$(ClO_4)_2$	40	Pink	8.59 (8.61)	10.34 (10.36)	36.83 (36.85)	4.99 (5.00)	20.43 (20.46)	115
4	[Ni(trpn)(abpt)]$(ClO_4)_2$	45	Violet	8.55 (8.57)	10.34 (10.36)	36.84 (36.86)	4.98 (5.00)	20.45 (20.47)	100
5	[Cu(trpn)(abpt)]$(ClO_4)_2$	35	Blue	9.20 (9.22)	10.27 (10.29)	36.58 (36.60)	4.95 (4.97)	20.30 (20.32)	113
6	[Zn(trpn)(abpt)]$(ClO_4)_2$	55	Colourless	9.44 (9.46)	10.24 (10.26)	36.49 (36.51)	4.93 (4.96)	20.25 (20.27)	107

Table 2
Infrared vibrational frequencies (cm^{-1}) of the complexes

	Compounds	ν(N–H)$_{trpn}$	δ(N–H)$_{trpn}$	ν(M–N)$_{trpn}$	ν(N–H)$_{abpt}$	Ring vibrations		ν(M–N)$_{abpt}$	ν(C=N)	Perchlorate $(ClO_4)_2^{2-}$ bands
						Out of plane ring deformation	In plane ring deformation			
1	[Mn(trpn)(abpt)]$(ClO_4)_2$	3295 s	1600 m	420 s	2935		604	225	1465 m	1081, 930
2	[Fe(trpn)(abpt)]$(ClO_4)_2$	3289 s	1585 m	425 s	2945		610	218	1480 m	1382, 932
3	[Co(trpn)(abpt)]$(ClO_4)_2$	3264 s	1580 m	431 s	2960	408	612	220	1490 m	1271, 940
4	[Ni(trpn)(abpt)]$(ClO_4)_2$	3185 s	1582 m	440 s	2980	412	607	215	1470 m	1360, 945
5	[Cu(trpn)(abpt)]$(ClO_4)_2$	3197 s	1589 m	410 s	2988	409	608	228	1485 m	1098, 937
6	[Zn(trpn)(abpt)]$(ClO_4)_2$	3256 s	1595 m	428 s	2971	415	605	235	1475 m	1189, 935

The ^{1}H NMR spectrum of the Zn(II) complex shows two triplets at 2.79 and 2.52 ppm corresponding to methylene protons adjacent to the primary amine (6H, CH_2–NH_2) and tertiary amine (6H, N–CH_2) protons of trpn, respectively [33]. Furthermore, a broad signal appearing around 1.28 ppm and a multiplet observed at 1.58 ppm may be assigned [33] to primary amine protons (6H, NH_2) and methylene protons (6H, C–CH_2–C) of the trpn moiety.

Chemical shifts of the protons of the pyridine ring coordinated to the metal atom are noticeably different from those observed for non-coordinating pyridine ring of the abpt ligand. The proton resonances of the coordinated pyridine ring are observed [2,4] at 8.51 ppm (d, H_{11}), 8.27 ppm (t, H_{10}), 7.51 ppm (t, H_9) and 8.57 ppm (d, H_8), while the resonances of the non-coordinated ring protons appeared at 7.29 ppm (d, H_{17}), 8.24 (t, H_{16}), 7.29 ppm (t, H_{15}) and 8.26 ppm (d, H_{14}). On the basis of these data it is possible to justify the corresponding downfield shift induced by the coordination of the pyridine nitrogen atom (N_7) to the metal atom. A broad signal appearing at 4.99 ppm may be attributed [34] to primary amine protons (N–NH_2, 2H) of the abpt ligand which is downfield shifted due to intramolecular H-bonding ($N_{13}\cdots N_1'$).

The observed magnetic moments and bands obtained in the electronic spectra of complexes of Mn(II), Co(II), Ni(II) and Cu(II) (Table 3) unambiguously suggest [35] an octahedral environment around the metal centres except Cu(II) where an octahedral distortion in the geometry has been found. The effective paramagnetic moment of Fe(II) in [Fe(trpn)(abpt)]$(ClO_4)_2$ calculated from susceptibility measurement at 298 K was found to be 5.45 B.M, corresponding to a high spin d^6 system, while on cooling the sample the μ_{eff} value decreases to 3.22 B.M at 80 K suggesting that the complex predominantly is a low spin one.

3.1. Single crystal structure of [Ni(trpn)(abpt)]$(ClO_4)_2$ (4)

A view of a [Ni(trpn)(abpt)]$(ClO_4)_2$ unit together with the atom labelling scheme is presented in Fig. 2.

The crystal structure consists of discrete [Ni(trpn)(abpt)]$^{2+}$ octahedral cations and $(ClO_4)_2^{2-}$ anions. From the crystal structure it is clear that the octahedral environment around the Ni(II) ion is composed of four nitrogen donors (N_{18}, N_{19}, N_{20}, N_{21}) from the trpn ligand and N_7 (pyridine ring) and N_4 atom (triazole ring) from the abpt ligand. The bond lengths and angles associated with the trpn ligand lie within the range reported [22,36] for tripodal tetramines.

In the free abpt ligand the angles N_4—C_5—C_6 and N_1—C_5—C_6 determining the position of the pyridine ring would be expected [1] to be about 126°. On complexation certain deformations occurs in the structure of

Table 3
Magnetic moment values, electronic spectral data and assignments

	Compound	μ_{eff} (B.M)	Band position (cm^{-1})	Assignments
1	[Mn(trpn)(abpt)](ClO$_4$)$_2$	5.81	26,495 19,685	$^6A_{1g} \rightarrow {}^4T_{2g}$ $^6A_{1g} \rightarrow {}^4T_{1g}$
2	[Fe(trpn)(abpt)](ClO$_4$)$_2$	5.45	11,642	$^5T_{2g} \rightarrow {}^5E_g$
3	[Co(trpn)(abpt)]ClO$_4$)$_2$	4.12	23,340 14,581	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
4	[Ni(trpn)(abpt)](ClO$_4$)$_2$	3.04	27,330 20,210 11,225	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$
5	[Cu(trpn)(abpt)](ClO$_4$)$_2$	1.78	19,460 16,390	$^2B_{1g} \rightarrow {}^2E_g$ $^2B_{1g} \rightarrow {}^2B_{2g}$

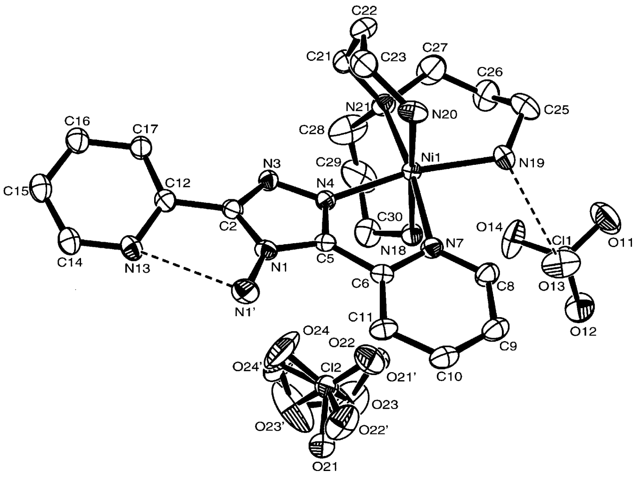


Fig. 2. An ORTEP drawing of [Ni(trpn)(abpt)](ClO$_4$)$_2$ with the numbering scheme.

the ligand, the angle N_4—C_5—C_6 is smaller [121.8 (4)°] than N_1—C_5—C_6 [129.5 (4)°].

4. Supplementary data

Supplementary data are available from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk), quoting the deposition number 201073.

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