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Synthesis and spectroscopic characterisation of cobalt(III) and nickel(II) complexes with 5-methyl-3-formylpyrazole-N(4)-dibutylthiosemicarbazone (HMP_zNBu_2): X-ray crystallography of $[Co(MP_zNBu_2)_2]NO_3\cdot H_2O$ (**I**) and $[Ni(HMP_zNBu_2)_2](ClO_4)_2$ (**II**)

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Abstract

New cobalt(III) and nickel(II) complexes of 5-methyl-3-formylpyrazole-N(4)-dibutylthiosemicarbazone (HMP_zNBu_2), $[Co(MP_zNBu_2)_2]X\cdot H_2O$ and $[Ni(HMP_zNBu_2)_2]X_2$ ($X = Cl$, Br, ClO_4, BF_4 and NO_3), respectively, have been synthesised and physico-chemically characterised by magnetic measurements (polycrystalline state), ^1H NMR [for Co(III) complexes], electronic and IR spectra. The reported species are all cationic complexes, behaving as 1:1 [for Co(III) complexes] and 1:2 [for Ni(II) complexes] electrolytes in MeOH. Electronic spectral features of the diamagnetic Co(III) and paramagnetic Ni(II) species classify them as six-coordinate distorted octahedral ones. IR spectra (4000–200 cm^{-1}) indicate a monoprotic tridentate (NNS) function of HMP_zNBu_2 coordinating to the central Co(III) via the pyrazolyl (tertiary) ring nitrogen, azomethine nitrogen and thiolato sulfur atom; while for the Ni(II) complexes, HMP_zNBu_2 behaves as neutral NNS tridentate, bonding to Ni(II) through the pyrazolyl iminic nitrogen, azomethine nitrogen and thioketo sulfur. ^1H NMR data (in DMSO-d_6 at 300 MHz) for the uncomplexed ligand and those of its Co(III) complexes are commensurate with the propositions of bonding sites envisaged from IR data. X-ray crystallographic data of **I** ($P\bar{1}$, triclinic) and of **II** ($C2/c$, monoclinic) have authenticated CoN_4S_2 and NiN_4S_2 octahedral coordination, respectively; in both **I** and **II**; the pair of coordinating ligands are nearly orthogonal to each other with the difference that while in **I**, the pair of ligands are monodeprotonated, in **II**, the same pair of ligands are neutral.

Keywords: Cobalt(III) complexes; Nickel(II) complexes; Synthesis; Spectroscopy; Thiosemicarbazone; X-ray crystallography

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1. Introduction

Heterocyclic thiosemicarbazones and their transition metal ion complexes have been researched extensively for the last two decades, primarily because of their wide range of potentially beneficial biological properties [1–5]. It is well authenticated that a NNS tridentate system is present in most of the thiosemicarbazones having carcinostatic potency [6] and possessing substantial in vitro activity against various human tumour lines [7,8]. Although the coordination chemistry of nickel(II) with pyridyl thiosemicarbazones has been widely studied [9], only a little work has been reported on nickel(II) complexes with heterocyclic thiosemicarbazones with pyrazole as the heterocyclic moiety [10–12]. As a part of our comprehensive efforts towards synthesis and characterisation of new metal ion materials containing bio-relevant pyrazolyl thiosemicarbazones and related ligands and in continuation of our earlier publication [13] this paper is intended to report the synthesis and spectroscopic characterisation of a host of Co(III) and Ni(II) complexes with the title ligand, HMP_zNBu_2

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together with the X-ray crystallography of $[Co(MP_zNBu_2)_2]NO_3 \cdot H_2O$ (**I**) and $[Ni(HMP_zNBu_2)_2](ClO_4)_2$ (**II**), pointing to a difference in the mode of bonding of the ligand towards Co(III) and Ni(II) salts.

2. Experimental

Solvents and reagents were of AR grade and were obtained from commercial sources and used as such without further purification. Spectrograde solvents were used for spectral and conductance measurements.

2.1. Preparation of 5-methyl-3-formylpyrazole-N(4)-dibutylthiosemicarbazone (HMP_zNBu_2)

The synthesis of the title ligand, 5-methyl-3-formylpyrazole-*N*(4)-dibutylthiosemicarbazone (HMP_zNBu_2) (Fig. 1), following a method similar to that reported earlier [10], but suitably modified, followed by the final transamination [14] of the *S*-methyldithiocarbazate of 5-methyl-3-formylpyrazole (HMP_zSMe) with dibutylamine, has been reported in an earlier communication [15]. White crystallised product (from ethanol) obtained with a yield of approximately 70%, melted at 155–157 °C.

Anal. Found: C, 57.0; H, 8.4; N, 24.0; Calc. for $C_{14}H_{25}N_5S$: C, 56.9; H, 8.4; N, 23.7%. ^1H NMR δ (DMSO-d_6) 2.41 (3H, s), 6.17 (1H, s), 7.29 (1H, s), 11.66(1H, b), 2.15 (4H, t), 1.67 (4H, m), 1.37 (4H, m), 0.93 (6H, t); EI MS: m/z 295 (M^+, 65%).

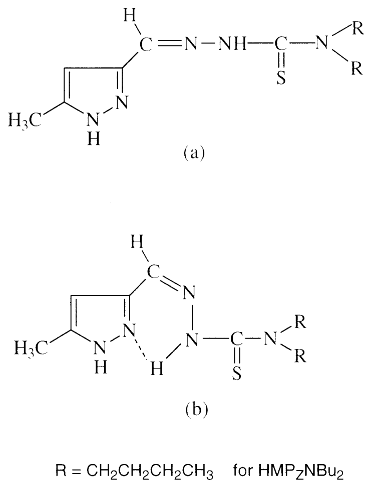

Fig. 1. Structural formulation of HMP_zNBu_2.

2.2. Preparation of the complexes

2.2.1. $[Co(MP_zNBu_2)_2]X \cdot H_2O$ and $[Ni(HMP_zNBu_2)_2]X_2$ (X = Cl, Br, ClO_4, BF_4 and NO_3)

The reported Co(III) and Ni(II) complexes were prepared by refluxing ethanolic solution of the ligand (1.05 mmol) and the corresponding hydrated Co(II) or Ni(II) salts (0.525 mmol) in a water bath for 1 h. On slow evaporation of the coloured solutions, the desired Co(III) or Ni(II) complexes crystallised out and were filtered off, washed with cold ethanol and were dried over anhydrous $CaCl_2$; the yield varied between 70 and 80%. Dark red brown crystals of $[Co(MP_zNBu_2)_2]NO_3 \cdot H_2O$ (**I**) and dark green crystals of $[Ni(HMP_zNBu_2)_2](ClO_4)_2$ (**II**) were found to be suitable for X-ray diffraction.

Note:

i) the ligand, HMP_zNBu_2, favours Co(II)→Co(III) transformation inducing oxidation as is known with similar ligand systems [16].
ii) Caution! Perchlorate compounds are potentially explosive and should be handled with care.

2.3. Physical measurements

The nickel contents of the complexes were determined gravimetrically as anhydrous dimethylglyoximatonickel(II). The methodology for determination of cobalt content of the complexes and different instrumental techniques adopted for characterisation of the complexes are similar as described earlier [13b,13d].

2.4. Structure determination

X-ray diffraction data of the complexes, collected on a Bruker P4 diffractometer using Mo Kα radiation, were corrected for Lorentz, polarisation and absorption effects. The structures were solved by direct methods and refined using the full-matrix least-squares method based on $|F_{obs}|^2$ [17]. The non-hydrogen atoms were refined anisotropically, while the hydrogen atoms, either located from difference electron density maps or generated using idealised geometry, were used in the structure factor calculations with isotropic thermal parameters. Neutral atom scattering factors [18] were used and anomalous dispersion effects were included in F_{calc} [19]. The crystallographic data are summarised in Table 4. The final positional and thermal parameters are available as supplementary material.

3. Results and discussion

3.1. Spectroscopic characterisation of HMP_zNBu_2

The title ligand, HMP_zNBu_2, has been characterised by elemental analyses (C, H and N), IR, ^1H NMR and mass spectrum and the results have been reported earlier [15].

3.2. Characterisation of the Co(III) and Ni(II) complexes

The reported Co(III) and Ni(II) complexes provide satisfactory C, H, N and metal analyses and conform to the general composition: $[Co(MP_zNBu_2)_2]X\cdot H_2O$ and $[Ni(HMP_zNBu_2)_2]X_2$ (X = Cl, Br, ClO_4, BF_4 and NO_3). The molar conductance values in MeOH (30 °C) classify the Co(III) complexes as 1:1 and Ni(II) complexes as 1:2 electrolytes [20] (Table 1). All the Co(III) complexes are diamagnetic (at ~300 K) as expected for a spin-paired d^6 ion, while the Ni(II) complexes are paramagnetic ($\mu_{eff} = 2.89–3.20$ BM) for a normal spin free d^8 system.

3.2.1. Spectral studies

The solid state electronic spectra (DRS) of all the reported cobalt(III) complexes are similar in nature and exhibit three bands in the regions 15 015–15 385, 20 690–21 685 and 23 695–24 155 cm^{-1} which may be assigned to $^1A_{1g} \rightarrow {}^3T_{2g}$, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions, respectively; the data are consistent with an overall octahedral symmetry. However, the electronic spectra in MeOH solution of these complexes show two bands in the regions 43 510–45 660 and 30 580–30 955 cm^{-1} which may be attributed to intraligand charge transfer bands ($\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, respectively). The spectra also exhibit a shoulder at 25 245–26 415 cm^{-1}, probably due to S → Co(III) charge transfer bands (LMCT). The spectra do not possess any d → d transition bands, which may be due to the masking of d → d bands by strong CT bands. The diffuse reflectance spectra of the Ni(II) complexes are characterised by three main bands in the regions 11 710–11 750 cm^{-1} [$^3A_{2g}$ (F) $\rightarrow {}^3T_{2g}$ (F)(ν_1)], 17 270–17 545 cm^{-1} [$^3A_{2g}$ (F) $\rightarrow {}^3T_{1g}$ (F)(ν_2)] and 27 175–27 740 cm^{-1} [$^3A_{2g}$ (F) $\rightarrow {}^3T_{1g}$ (P)(ν_3)], which correspond to an overall octahedral symmetry.

The solution spectra (in MeOH) of these complexes are similar in nature and show two bands in the regions 11 125–11 780 cm^{-1} (ν_1) and 17 210–17 360 cm^{-1} (ν_2), which are not significantly different from the bands in the solid state; indicating that no gross electronic or geometric change occurs on dissolution of the complexes in the said solvent. The ν_3 band, in all cases, are found to appear in the UV region where they might be masked by an intense internal $\pi \rightarrow \pi^*$ transition of the ligand or intense CT absorption bands [10,12]. The characteristic IR bands (400–200 cm^{-1}) for the free ligand, HMP_zNBu_2, when compared with those of its Co(III) and Ni(II) complexes, provide significant indications with regard to the bonding sites of the primary ligand molecule (Table 2). A negative shift in $\nu_{(CH=N)}$ band (1615 cm^{-1}) in the free ligand spectrum to the lower value (1585–1600 cm^{-1}) in its complexes indicate coordination of the azomethine nitrogen to the central metal ion; the IR bands at 460–490 cm^{-1} in the complexes are then assignable to $\nu_{(M-N)}$ [13,9,12]. IR bands at 1510 and 625 cm^{-1} in the free ligand spectrum, assignable to $\nu_{(C=N)}$ (pyrazole ring) and the in-plane deformation of the pyrazole ring, respectively, have been found to shift to the higher frequency region, pointing to the participation of the tertiary ring nitrogen atom (^2N) as a potential bonding site [9,13,21]. The presence of bands at 272–286 cm^{-1} in the complexes are clearly assignable to $\nu_{(M-N)}$ (pyrazole ring) [13,9]. An intense band at 865 cm^{-1} in the free ligand spectrum, assigned to $\nu_{(C=S)}$ has been found to shift to lower frequency regions (775–798 cm^{-1}) in the complexes, indicating the coordination of the thiol/thione sulfur to metal ion;

Table 1
Elemental analyses, colours and other pertinent physico-chemical properties of the complexes

Complex (colour)	Elemental analyses Found (Calc.)				Conductivity at 30 °C (Ω^{-1} cm^2 mol^{-1})	μ_{eff} (BM) at 300 K
	% C	% H	% N	% M		
$[Co(MP_zNBu_2)_2]Cl\cdot H_2O$ (red brown)	48.0 (47.9)	7.1 (7.1)	19.7 (19.9)	8.4 (8.4)	90	dia
$[Co(MP_zNBu_2)_2]Br\cdot H_2O$ (dark brown)	45.0 (45.1)	6.7 (6.7)	18.9 (18.9)	7.8 (7.9)	95	dia
$[Co(MP_zNBu_2)_2]ClO_4\cdot H_2O$ (dark red brown)	43.8 (44.0)	6.5 (6.5)	18.3 (18.3)	7.6 (7.7)	112	dia
$[Co(MP_zNBu_2)_2]BF_4\cdot H_2O$ (red brown)	44.9 (44.7)	6.6 (6.6)	18.5 (18.6)	7.8 (7.8)	109	dia
$[Co(MP_zNBu_2)_2]NO_3\cdot H_2O$ (red brown)	46.4 (46.2)	6.8 (6.9)	21.2 (21.2)	8.0 (8.1)	85	dia
$[Ni(HMP_zNBu_2)_2]Cl_2$ (dark green)	46.5 (46.7)	6.9 (6.9)	19.7 (19.5)	8.1 (8.2)	205	2.89
$[Ni(HMP_zNBu_2)_2]Br_2$ (olive green)	41.3 (41.6)	6.2 (6.2)	17.4 (17.3)	7.3 (7.3)	178	3.18
$[Ni(HMP_zNBu_2)_2](ClO_4)_2$ (dark green)	39.7 (39.6)	5.9 (5.9)	16.7 (16.5)	6.9 (6.9)	198	3.07
$[Ni(HMP_zNBu_2)_2](BF_4)_2$ (blue green)	41.2 (40.9)	6.2 (6.1)	17.2 (17.0)	7.2 (7.1)	170	2.97
$[Ni(HMP_zNBu_2)_2](NO_3)_2$ (light green)	43.5 (43.5)	6.5 (6.5)	21.9 (21.7)	7.7 (7.6)	178	3.20

Table 2
IR assignments (cm^{-1}) for the ligand (HMP_zNBu_2) and complexes pertaining to coordination sites

Compound	$\nu_{(CH=N)}$ (azomethine)	$\nu_{(C=N)}$ (pyrazole)	$\nu_{(C=S)}$	$\nu_{(M-N)}$ (azomethine)	$\nu_{(M-N)}$ (pyrazole)	$\nu_{(M-S)}$
HMP_zNBu_2	1615	1510	865			
$[Co(MP_zNBu_2)_2]Cl \cdot H_2O$	1595	1530	798	460	272	348
$[Co(MP_zNBu_2)_2]Br \cdot H_2O$	1592	1537	782	468	280	360
$[Co(MP_zNBu_2)_2]ClO_4 \cdot H_2O$	1600	1532	775	478	278	355
$[Co(MP_zNBu_2)_2]BF_4 \cdot H_2O$	1598	1535	780	467	285	375
$[Co(MP_zNBu_2)_2]NO_3 \cdot H_2O$	1590	1540	778	465	275	355
$[Ni(HMP_zNBu_2)_2]Cl_2$	1585	1540	785	485	280	365
$[Ni(HMP_zNBu_2)_2]Br_2$	1587	1545	775	490	276	370
$[Ni(HMP_zNBu_2)_2](ClO_4)_2$	1595	1540	790	480	280	375
$[Ni(HMP_zNBu_2)_2](BF_4)_2$	1592	1540	797	476	285	360
$[Ni(HMP_zNBu_2)_2](NO_3)_2$	1590	1548	789	490	275	375

moreover, the appearance of a new band in the region (348–375 cm^{-1}) in the complexes is assignable to $\nu_{(M-S)}$ [13,22,23].

A comparison of the ^1H NMR spectral data for the Co(III) complexes and those of the free ligand (Table 3) gives rise to the following points. (i) The peaks $\delta = 12.65$ and 11.66 due to imino ^2NH (at the thiosemicarbazone part) in the free ligand disappear after complexation, indicating that the ligand suffers deprotonation and coordinates to the Co(III) ion through the thiol sulfur. (ii) The signals for the terminal $N(n\text{-}Bu_2)_2$ groups show a slight down-field shift on going from the ligand to complexes; this indicates the coordination of the thiol sulfur to Co(III) ion, which results in reduction of electron density of the terminal N-atom of $N(n\text{-}Bu_2)_2$. (iii) The azomethine CH proton exhibiting a peak at $\delta = 7.29$ in the free ligand, suffers maximum downfield shift in the complexes ($\delta = 7.53–7.63$), indicating the coordination of the azomethine nitrogen to the central Co(III) ion. (iv) A down-field shift of ^4CH (pyrazole ring) from $\delta = 6.17$ (free ligand) to $\delta = 6.25–6.32$ in the complexes is consistent with the coordination of the pyrazole ring ^2N (tertiary) to the Co(III) ion.

^1H NMR spectral studies, thus, provide support for the bonding characteristics of the primary ligand system (HMP_zNBu_2) in forming complexes with Co(III) through pyrazolyl ring nitrogen ^2N (tertiary), azomethine nitrogen and thiolato sulfur atom [13], as suggested by the IR spectroscopic data.

*3.3. Crystal structures of $[Co(MP_zNBu_2)_2]NO_3 \cdot H_2O$ (**I**) and $[Ni(HMP_zNBu_2)_2](ClO_4)_2$(**II**)*

ORTEP [24] diagrams of the complexes (**I** and **II**) together with the atom numbering schemes are shown in Fig. 2(a and b). In both the complexes, the metal ions, Co(III)/Ni(II), have distorted octahedral coordination, with the distortion being more pronounced in the Ni(II) complex (Table 5). In complex **I**, a pair of monodeprotonated ligands ($MP_zNBu_2^-$) coordinate to the Co(III) ion through the thiolato sulfur atoms [S(1A), S(1B)], the pyrazolyl (tertiary) ring nitrogen atoms [N(1A), N(1B)] and the hydrazinic chain nitrogen atoms [N(3A), N(3B)]. In complex **II**, the coordination is similar with the difference that the pair of coordinating ligands are not deprotonated. The crystallographic asymmetric unit in complex **I** consists of a $[Co(MP_zNBu_2)_2]^+$ cation, a NO_3^- anion and a molecule of water of crystallisation. In complex **II**, the cation $[Ni(HMP_zNBu_2)_2]^{++}$ straddles a twofold symmetry axis with the Ni(II) ion located

Table 3
^1H NMR data (in DMSO-d_6) for HMP_zNBu_2 and its Co(III) complexes relative to TMS

Compound	–N*H* (imino)	azomethine –C–*H*	Ring (P_z) $^1N–H$	Ring (P_z) $C_5–CH_3$	Ring (P_z) $C_4–H$	$–N–(CH_2–C_3)_2$	$–N–(C–CH_2–C_2)_2$	$–N–(C_2–CH_2–C)_2$	$–N(C_3–CH_3)_2$
HMP_zNBu_2	12.65 11.66	7.29	13.12	2.41	6.17	2.15	1.67	1.37	0.93
$[Co(MP_zNBu_2)_2]Cl \cdot H_2O$		7.60	13.26	2.48	6.28	2.18	1.73	1.41	0.97
$[Co(MP_zNBu_2)_2]Br \cdot H_2O$		7.63	13.30	2.47	6.25	2.20	1.72	1.40	1.02
$[Co(MP_zNBu_2)_2]ClO_4 \cdot H_2O$		7.58	13.28	2.50	6.28	2.21	1.73	1.43	1.05
$[Co(MP_zNBu_2)_2]BF_4 \cdot H_2O$		7.53	13.33	2.47	6.29	2.25	1.71	1.40	0.99
$[Co(MP_zNBu_2)_2]NO_3 \cdot H_2O$		7.61	13.40	2.50	6.31	2.22	1.70	1.42	0.98

Table 4
Crystal data

	$[Co(MP_zNBu_2)_2]^+NO_3^-\cdot H_2O$ (**I**)	$[Ni(HMP_zNBu_2)_2]^{++}2ClO_4^-$ (**II**)
Empirical formula	$C_{28}H_{50}CoN_{11}O_4S_2$	$C_{28}H_{50}Cl_2NiN_{10}O_8S_2$
Crystal colour	reddish brown	dark green
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$
Unit cell dimensions		
a (Å)	8.567(2)	23.923(2)
b (Å)	11.477(4)	14.923(1)
c (Å)	19.568(4)	13.484(2)
α (°)	82.81(2)	
β (°)	83.86(2)	119.09(1)
γ (°)	76.19(2)	
Volume (Å^3)	1847.8(9)	4206.9(7)
Z	2	4
D_{calc} (g cm^{-3})	1.308	1.340
Crystal habit	Plate	Chunk
Crystal size (mm)	0.09 × 0.70 × 0.32	0.33 × 0.61 × 0.48
θ Range for data collection (°)	2.5–25.0	2.0–27.5
Index ranges	$0 \leq h \leq 10$, $-13 \leq k \leq 13$, $-23 \leq l \leq 23$	$0 \leq h \leq 31$, $0 \leq k \leq 19$, $-17 \leq l \leq 15$
Reflections collected	6964	4952
Independent reflections	6493 [$R_{int} = 0.019$]	4841 [$R_{int} = 0.022$]
Absorption correction	SHELXA	SHELXA
Max/min transmission	0.8681, 0.5679	0.7468, 0.3111
Refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Observed reflectons [$I > 2\sigma(I)$]	4216	3395
Number of parameters	474	290
Number of restraints	34	25
Goodness-of-fit on F^2	1.05	1.02
Final R indices [$I > 2\sigma(I)$] [a]	$R_1 = 0.0736$, $wR_2 = 0.2072$	$R_1 = 0.0597$, $wR_2 = 0.1605$
Final R indices (all data)	$R_1 = 0.1108$, $wR_2 = 0.2381$	$R_1 = 0.0858$, $wR_2 = 0.1779$
Largest difference peak and hole (e Å^{-3})	0.898 and −0.487	0.611 and −0.502

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = \{\Sigma[(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $a = 0.1302$ and $b = 1.8548$ for (**I**), and $a = 0.0955$ and $b = 5.3757$ for (**II**), and $P = (F_o^2 + 2F_c^2)/3$.

on the axis. This results in a crystallographic asymmetric unit consisting of half a metal ion, one unit of the HMP_zNBu_2 ligand and a disordered ClO_4^- as counter ion.

In complex **I**, two molecules (designated as A and B) of the tridentate ligand [5-methyl-3-formylpyrazole-*N*(4)-dibutylthiosemicarbazone] coordinate to the Co(III) ion to form four five-membered chelate rings [Co–S(1A)–C(6A)–N(4A)–N(3A), Co–S(1B)–C(6B)–N(4B)–N(3B), Co–N(1A)–C(4A)–C(5A)–N(3A) and Co–N(1B)–C(4B)–C(5B)–N(3B)]. The two azomethine nitrogen atoms, N(3), are *trans* to each other, while the pyrazolyl ring nitrogen atoms, N(1), and the sulfur atoms, S(1), are in the *cis* positions. The coordination of the tridentate ligand in complex **II** is identical, except that we do not refer to the individual members of the pair of ligands as they are related by symmetry.

The deprotonation of the hydrazinic nitrogens, N(4A) and N(4B), in complex **I** results in narrowing of the endocyclic angles at these atoms compared with the corresponding angle in complex **II**, where the hydrazinic nitrogen atom is not deprotonated (Table 5). At the same time, the double bond character of the N(4)–C(6) bond in complex **I** is enhanced with a corresponding decrease in the double bond character of the C(6)–S(1) bond; this trend is not observed in the case of complex **II** where deprotonation does not occur.

In both the complexes, the shortening of the bond distances of the metal ions with the azomethine nitrogen atoms, N(3), relative to the bond distances with the pyrazolyl (tertiary) ring nitrogen atoms, N(1) (Table 5), may be attributed to the fact that the azomethine nitrogen is a stronger base compared with the pyrazolyl nitrogen.

The tridentate ligands in both the complexes are more or less planar. In complex **I**, C(6A) and C(5A) in ligand A, and N(4B) and C(3B) in ligand B, have the largest deviations in opposite directions of +0.117(6), −0.066(6), +0.099(6), and −0.216(6) Å, respectively, from the least-squares mean planes through Co–S(1)–C(6)–N(4)–N(3)–C(5)–C(4)–C(3)–C(2)–N(2)–N(1). For the single crystallographically independent ligand in

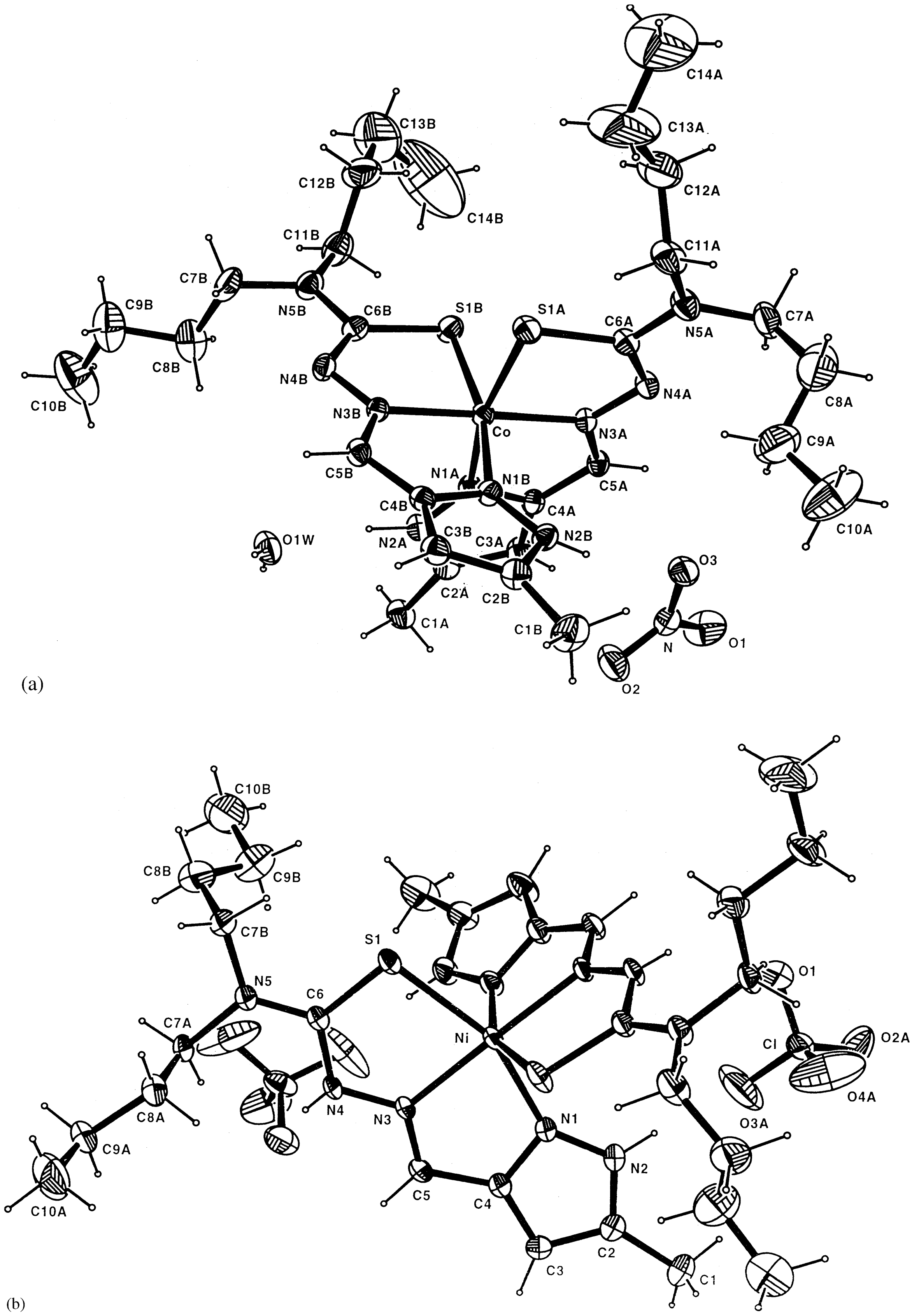

Fig. 2. (a) ORTEP diagram of [Co(MP$_z$NBu$_2$)$_2$]NO$_3$·H$_2$O (**I**) showing the atom numbering scheme. (b) ORTEP diagram of [Ni(HMP$_z$NBu$_2$)$_2$](ClO$_4$)$_2$ (**II**) showing the atom numbering scheme.

complex **II**, the maximum deviations from planarity of the tridentate ligand are exhibited by N(1) [+0.124(3) Å] and C(2) [−0.353(6) Å]. In both the complexes, the pair of coordinating ligands are nearly orthogonal to each other; the dihedral angle between ligand A and ligand B is 86.72(3)° in complex **I**; in complex **II**, the dihedral angle between the ligand and its twofold related counterpart is 98.68(2)°. The three individual rings in both the structures, namely the pyrazole and the two five-membered chelate rings, are individually almost planar with small dihedral angles between them. In complex **I**, the maximum dihedral angle of 8.2(2)° is between the pyrazole ring N(1B)–N(2B)–C(2B)–C(3B)–C(4B) and the chelate ring Co–N(1B)–C(4B)–C(5B)–N(3B); in complex **II**, the rings N(1)–N(2)–C(2)–C(3)–C(4) and Ni–N(3)–S(1)–C(6)–N(4) have the maximum dihedral angle of 14.88(1)°.

Table 5
Selected bond distances (Å) and angles (°), with e.s.d.s in parentheses, of $[Co(MP_zNBu_2)_2]^+NO_3^-\cdot H_2O$ (**I**) and $[Ni(HMP_zNBu_2)_2]^{++}$-$2ClO_4^-$ (**II**)

Complex **I**	Ligand A	Ligand B	Complex **II** [a]	
Bond lengths				
Co–S(1)	2.218(2)	2.209(2)	Ni–S(1)	2.387(1)
Co–N(1)	1.946(4)	1.944(4)	Ni–N(1)	2.112(3)
Co–N(3)	1.899(5)	1.909(5)	Ni–N(3)	2.037(3)
N(4)–C(6)	1.328(8)	1.325(8)	N(4)–C(6)	1.355(5)
C(6)–S(1)	1.745(6)	1.742(7)	C(6)–S(1)	1.699(4)
Bond angles				
S(1A)–Co–N(1A)		167.03(15)	S(1)–Ni–N(1)	158.10(9)
S(1B)–Co–N(1B)		167.54(15)	S(1)–Ni–N(3)	81.08(8)
S(1A)–Co–N(3A)		85.19(14)	S(1)–Ni–N(1)′	88.24(8)
S(1B)–Co–N(3B)		85.65(14)	S(1)–Ni–N(3)′	101.46(8)
S(1A)–Co–N(1B)		89.16(14)	N(1)–Ni–N(3)	77.08(11)
S(1B)–Co–N(1A)		90.17(14)	N(1)–Ni–N(3)′	100.28(11)
S(1A)–Co–N(3B)		94.13(14)	N(1)–Ni–N(1)′	94.09(11)
S(1B)–Co–N(3A)		96.04(14)	N(3)–Ni–N(3)′	176.20(12)
N(1A)–Co–N(3A)		81.86(19)	S(1)–Ni–S(1)′	97.68(4)
N(1B)–Co–N(3B)		81.89(19)	N(3)–N(4)–C(6)	119.0(3)
N(1A)–Co–N(3B)		98.80(19)		
N(1B)–Co–N(3A)		96.42(19)		
N(1A)–Co–N(1B)		91.63(18)		
N(3A)–Co–N(3B)		178.19(19)		
S(1A)–Co–S(1B)		91.85(7)		
N(3A)–N(4A)–C(6A)		111.5(5)		
N(3B)–N(4B)–C(6B)		111.5(5)		

[a] The primed atoms are related to the corresponding atoms in the asymmetric unit by the symmetry operation 1−*x*, *y*, 1/2−*z*.

Table 6
Hydrogen bonding distances (Å) and angles (°), including C–H···X contacts

D–H···A	D–H	D···A	H···A	∠D–H···A
Complex I				
N(2A)–H(2A)···O(1W)	0.93(6)	2.792 (8)	1.87(6)	167(5)
N(2B)–H(2B)···O(3)	0.81(7)	2.823(8)	2.03(7)	166(5)
O(1W)–H(11W)···O(2)^{i}	0.75(11)	2.895(10)	2.17(11)	165(14)
O(1W)–H(12W)···O(1)^{ii}	0.69(8)	2.848(11)	2.19(8)	162(8)
C(1A)–H(1AA)···O(2)^{i}	0.96	3.302(10)	2.58	132
C(3A)–H(3AA)···O(1)^{iii}	0.93	3.318(9)	2.59	135
C(7A)–H(7AB)···N(4A)	0.97	2.681(9)	2.20	109
C(9A)–H(9AA)···O(3)	0.97	3.403(12)	2.56	146
C(11A)–H(11B)···S(1A)	0.97	2.979(7)	2.49	111
C(11B)–H(11D)···S(1B)	0.97	2.967(8)	2.53	108
C(7B)–H(7BB)···N(4B)	0.97	2.730(9)	2.39	100
Complex II				
N(2)–H(2)···O(3A)	0.86	2.668(6)	1.82	168
N(4)–H(4)···O(1)^{iv}	0.70(5)	3.143(5)	2.51(5)	152(4)
C(7A)–H(7AB)···O(2A)^{v}	0.97	3.277(8)	2.56	131
C(5)–H(5A)···O(1)^{iv}	0.93	3.371(5)	2.59	142
C(7B)–H(7BA)···S(1)	0.97	3.014(6)	2.47	115

Symmetry equivalents, (i) 1−*x*, 1−*y*, −*z*; (ii) −1+*x*, *y*, *z*; (iii) 2−*x*, 1−*y*, −*z*; (iv) −1/2+*x*, 1/2−*y*, −1/2+*z*; (v) −1/2+*x*, 1/2+*y*, −1+*z*.

Table 6 gives the details of the hydrogen bonding and C–H···X hydrogen bond-like contacts. It is interesting to note that, in both the complexes, one of the butyl chain carbon atoms, from both the coordinating ligands, forms a C–H···S contact [C(11A)–H(11B)···S(1A) and C(11B)–H(11D)···S(1B) in complex **I**, and C(7B)–H(7BA)···S(1) in complex **II**] which restricts free rotation of the dibutyl moiety about the C(6)–N(5) bond and fixes the conformation of the side chain. This is illustrated by the similarity in torsion angles about the C(6)–N(5) bond (Table 7). In both the structures, all the potential hydrogen donors, namely, the pyrazolyl secondary nitrogens, the water oxygen in complex **I**, and the hydrazinic nitrogen in complex **II**, are involved in classical hydrogen bond formation with the water, nitrate and perchlorate oxygen atoms.

4. Supplementary material

Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 188747 and 188748. Copies of this information may be obtained free of charge from The Director, CCDC Data Centre, 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).

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Table 7
Selected torsion angles (°)

Complex **I**		Complex **II**	
C(11A)–N(5A)–C(6A)–N(4A)	−175.0(6)	C(7B)–N(5)–C(6)–N(4)	177.9(4)
C(11B)–N(5B)–C(6B)–N(4B)	−174.4(6)	C(7B)–N(5)–C(6)–S(1)	−1.0(5)
C(11A)–N(5A)–C(6A)–S(1A)	5.3(9)	C(7A)–N(5)–C(6)–N(4)	6.3(5)
C(11B)–N(5B)–C(6B)–S(1A)	7.6(9)	C(7A)–N(5)–C(6)–S(1)	−172.6(3)
C(7A)–N(5A)–C(6A)–N(4A)	−4.9(9)		
C(7B)–N(5B)–C(6B)–N(4B)	−5.0(9)		
C(7A)–N(5A)–C(6A)–S(1A)	175.4(5)		
C(7B)–N(5B)–C(6B)–S(1B)	177.0(5)		

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