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Transition Metal Coordination Compounds of Two Pyrazole-substituted Ammonia Ligands. X-ray Structure of [Bis{bis(1-pyrazolylmethyl)amine}cobalt(II)]bis(nitrate)

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Abstract

The synthesis, spectroscopy and structure of mononuclear transition metal coordination compounds of the ligands tris(1-pyrazolylmethyl)amine (amtp) and bis(1-pyrazolylmethyl)amine (am2p) are described. In the compounds $M(amtp)X_2(H_2O)_n$, with $M = Co^{2+}$, Ni^{2+}, Cu^{2+} and/or Zn^{2+}, $X = Cl^-$, NCS^- and/or NO_3^-, and $n = 0$ or 1, the anions take part in the coordination of the metal ion resulting in penta- or hexa-chromophores. In the compounds $M_3(amtp)_2X_6$ with $M = Co^{2+}$, Cu^{2+} and Zn^{2+}, and $X = Cl^-$ and NCS^-, autoanion formation occurs, resulting in $[M(amtp)X]_2[MX_4]$ with both five-coordinated and four-coordinated metal ions. In these compounds the ligand acts as a tetradentate tripodal ligand.

Partial hydrolysis of amtp in its solutions with some of the metal salts results in the formation of am2p compounds. Octahedral complexes $M(am2p)_2(X)_2$ with $M = Co^{2+}$ and Ni^{2+}, and $X = Cl^-$ and NO_3^- are formed. With copper the compounds $Cu(am2p)(X)_2(H_2O)_n$ with $X = Cl^-$ ($n = 1$) and NO_3^- ($n = 0$), and $Cu(am2p)(pz)X_2(H_2O)$ with $X = Cl^-$, NCS^- and NO_3^- and pz = pyrazole are formed.

The compound $[Co(am2p)_2](NO_3)_2$ crystallizes in the orthorhombic space group *Fdd*2 with $a = 29.623(3)$, $b = 19.075(5)$, $c = 8.342(6)$ Å, $Z = 8$. The structure was solved by heavy-atom methods and refined by least-squares methods to a residual R of 0.038 ($R_w = 0.047$) for 1236 significant reflections. The asymmetric unit comprises half the formula unit with cobalt on a special position (twofold axis). The Co(II) ion is octahedrally surrounded by four pyrazole and two amine nitrogens of two symmetry related am2p ligands with distances of 2.088(5) and 2.087(4) Å to the pyrazole nitrogens and 2.229(5) Å to the amine nitrogen. The H atoms of the amine nitrogens are weakly hydrogen bonded to the nitrate anions in the lattice.

Introduction

The ligand tris(1-pyrazolylmethyl)amine (abbreviated amtp) [1] has a configuration similar to the configurations of the uninegative poly(1-pyrazolyl) borates and the neutral poly(1-pyrazolyl)methanes [2, 3]. Apart from the pyrazole N atoms, which constitute the only donor atoms in the polypyrazolylborates and -methanes, the poly(1-pyrazolyl)amines also possess an amine N atom which may [4, 5], or may not [6], coordinate.

Tris(1-pyrazolyl)borates usually form octahedral complexes in contrast to the pyrazole-substituted amine ligands investigated sofar. This is a consequence of the coordination participation of the amine N atom, whereby the N-pyrazole to N-amine bite of the ligand is too small to accommodate coordination angles of 90° or larger [5, 7]. In analogy with the pyrazolylborates, partly pyrazole-substituted amine ligands can also be obtained, either directly [8] or, like bis(1-pyrazolylmethyl)amine (abbreviated am2p), as hydrolysis products of higher pyrazole-substituted amine ligands [7, 9].

In the present paper we report the synthesis and spectroscopic characterization of several metal(II) amtp and am2p compounds and the X-ray crystal structure determination of the representative compound $[Co(am2p)_2](NO_3)_2$.

Experimental

Starting Materials and Syntheses

The synthesis of the ligand tris(1-pyrazolylmethyl)amine (amtp) was performed by a modification of the method reported earlier [1]. A slight excess of 1-(hydroxymethyl)pyrazole (0.43 mol) was stirred for 36 h at room temperature with ammonium acetate (0.14 mol) in 100 ml of acetonitrile. The organic solvent was then removed under reduced pressure, rendering a colourless oil. The oil, dissolved in trichloromethane, was washed once with 0.2 M NaOH and twice with water. After removing the solvent on a rotary evaporator, the oil was stored in

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an evacuated desiccator. After several days colourless crystals had grown in the oil: melting point 54–55 °C; NMR (^1H) signals: singlet at 5.23 ppm (6H), representing the methylene bridges, triplet at 6.22 ppm (3H) and doublets at 7.45 ppm at 7.62 ppm (both 3H), representing the pyrazole hydrogens (solvent DMSO-d_6).

Metal thiocyanates were prepared from the metal nitrates and ammonium thiocyanate. All other chemicals were commercially available, of sufficient purity, and used without further treatment.

The coordination compounds with amtp were prepared by dissolving the appropriate hydrated metal salt (2.5, 1.67, or 1.25 mmol, depending on the metal to ligand preparation ratio) in 12.5 ml ethanol and dissolving the ligand amtp (2.5 mmol) in 2.5 ml ethanol and combining the solutions. Occasionally triethylorthoformate was added to both solutions for dehydration before combining them. After precipitation, in some cases only after evaporization of part of the solvent, the products were collected by filtration and washed with ethanol. The coordination compounds with bis(1-pyrazolylmethyl)amine (am2p) precipitated from solutions of amtd containing certain metal salts, through partial hydrolysis of amtp.

Characterization Methods

Metal analyses were carried out complexometrically using EDTA as complexing agent and chloride was determined potentiometrically with $AgNO_3$ as the precipitating agent [10]. C, H and N analyses were performed at University College, Dublin.

Infrared spectra in the range 4000–200 cm^{-1} were recorded on a Perkin-Elmer 580 spectrophotometer, equipped with a PE Data Station as Nujol mulls between KRS-5 discs or as KBr pellets.

Solid-state electronic spectra (30 000–5000 cm^{-1}) were recorded on a Perkin-Elmer 330 spectrophotometer fitted with a diffuse reflectance attachment, using MgO as a reference.

EPR spectra of the powdered compounds were measured with a Varian E3 X-band spectrophotometer at room temperature and at 77 K (liquid nitrogen).

Proton nuclear magnetic resonance spectra were recorded on a JEOL PS-100 instrument employing a frequency of 99.5 MHz, using $SiMe_4$ as internal standard.

X-ray powder diffraction diagrams of the compounds were obtained with a Guinier-type camera using Cu Kα radiation. The samples were protected from atmospheric vapour by adhesive tape.

The conductivity of 10^{-3} M solutions in nitromethane (specific conductance 2.0×10^{-6} cm^{-1} Ω^{-1}) was measured at 20.0 ± 0.1 °C on a Philips PR 9500 conductometer (cell constant 1.47).

X-ray Methods and Structure Determination

A pink needle (0.7 × 0.2 × 0.2 mm) of $[Co(C_8H_{11}N_5)_2](NO_3)_2$, $M_r = 537.36$ mounted in a glass capillary, was subjected to graphite-monochromatized Mo(Kα) radiation ($\lambda = 0.71073$ Å) on a four-circle Enraf-Nonius CAD4 diffractometer, operated in the w/θ mode. Orthorhombic space group $Fdd2$. Cell dimensions from the setting angles of 24 reflections ($10° < \theta < 12°$): $a = 29.623(3)$, $b = 19.075(5)$, $c = 8.342(6)$ Å; $Z = 8$; $D_{calc} = 1.50$ g cm^{-1}; $F(000) = 2218$. Intensities were corrected for Lorentz and polarization effects. No absorption correction was applied as $\mu = 7.762$ cm^{-1} and transmission coefficients from 96.2 to 104.2. The scanning rate was adjusted to the required precision of $\sigma(I)/I = 0.01$ with a maximum scan time of 60 s per reflection. The instrument and crystal stability were checked every 5400 s of radiation time by measuring three reference reflections, $-2, 10, 0$; $4, 10, -2$; $6, -2, -4$; no significant changes in the intensities were observed. Ranges: $2.0° < \theta < 27.5°$, $-10 < h < 38$, $0 < k < 24$, $-10 < l < 10$. A total of 2887 independent reflections were measured of which 1236 with $I > 2\sigma(I)$ were used for the structure solution and refinement. The principal computer programs used in the crystallographic calculations were written or modified by Mrs E. Rutten-Keulemans and Dr R. A. G. de Graaff.

The position of the cobalt atom was determined from a Patterson map. The positions of the other non-hydrogen atoms were obtained using the program AUTOFOUR [11]. The atomic scattering factors were taken from ref. 12. Standard least-squares refinement. The non-hydrogen atoms were refined anisotropically. The function minimized was $\Sigma w|F_o - F_c|^2$ with $w = 1/\sigma^2(F)$. Most H atom positions were found from difference Fourier maps. The other H atoms were placed at 0.95 Å of their parent atom. The positional parameters of the H atoms were coupled to their parent atoms during the refinement stages. The temperature factors of the H atoms were coupled to one another and refined isotropically with a final B_{eq} value of 4.6 Å^2. At the final stage the conventional discrepancy index $R_F = \Sigma(|F_o - F_c|)/\Sigma F_o$ had been reduced to 0.038 and the weighted factor $R_w = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{1/2}$ to 0.046. Maximum positive and negative densities in the final difference Fourier are 0.63 and -0.89 e Å^{-3} respectively. Estimated standard deviations were calculated with the use of a correlation matrix.

Results and Discussion

General

Stoichiometries, melting points, colours and the proposed chromophores of the compounds with tris(1-pyrazolylmethyl)amine (amtp) and bis(1-

TABLE 1. Stoichiometries, melting points (°C), colours, and proposed chromophores of the amtp and am2p compounds

$Co(amtp)Cl_2(H_2O)$	99–101	purple	CoN_4Cl
$Ni(amtp)Cl_2(H_2O)$	212–215	blue–green	NiN_4Cl_2
$Cu(amtp)Cl_2(H_2O)$	172 d.	blue	CuN_4Cl_2
$Zn(amtp)Cl_2$	200–202	white	ZnN_4Cl_2
$Co(amtp)(NCS)_2$	180–182	purple	$CoN_4(NCS)$
$Ni(amtp)(NCS)_2$	248–250	blue	$NiN_4(NCS)_2$
$Cu(amtp)(NCS)_2$	137–139	green	$CuN_4(NCS)_2$
$Co(amtp)(NO_3)_2$	182 d.	purple	CoN_4O
$Zn(amtp)(NO_3)_2(H_2O)$	172–173	white	ZnN_4O
$Co_3(amtp)_2Cl_6$	185–187	deep blue	CoN_4Cl, $CoCl_4$
$Cu_3(amtp)_2Cl_6$	112–114	green	CuN_4Cl, $CuCl_4$
$Zn_3(amtp)_2Cl_6$	205–206	white	ZnN_4Cl, $ZnCl_4$
$Co_3(amtp)_2(NCS)_6$	206–208	deep blue	$CoN_4(NCS)$, $Co(NCS)_4$
$Zn_3(amtp)_2(NCS)_6$	198–199	white	$ZnN_4(NCS)$, $Zn(NCS)_4$
$Ni(am2p)_2Cl_2$	225 d.	violet	NiN_6
$Co(am2p)_2(NO_3)_2$	176–178	orange	CoN_6
$Ni(am2p)_2(NO_3)_2$	218–220	violet	NiN_6
$Cu(am2p)Cl_2(H_2O)$	168–170	light blue	CuN_3Cl_2 or CuN_3ClO
$Cu(am2p)(NO_3)_2$	175–178	light blue	CuN_3O_2
$Cu(am2p)(pz)Cl_2(H_2O)_2$	195–196	dark blue	CuN_4Cl
$Cu(am2p)(pz)(NO_3)_2(H_2O)$	148–150	dark blue	CuN_4O
$Cu(am2p)(pz)(NCS)_2(H_2O)_2$	132–133	green	$CuN_4(NCS)_2$

d. = decomposition.

pyrazolylmethyl)amine (am2p) are given in Table 1. All compounds gave satisfactory elemental analyses (see 'Supplementary Material'). Only the compound $Co_3(amtp)_2(NCS)_6$ and the compound $Zn_3(amtp)_2(NCS)_6$ are isomorphous. No other isomorphism could be established from the X-ray powder diffraction patterns. The infrared spectra of all compounds, although characteristic for pyrazole derivatives [13], differ in many details, which also indicates that these compounds span a large structural variety.

The amtp Compounds

Two different types of compounds (see Table 1) were obtained for the cobalt, copper and zinc chlorides and thiocyanates by using different metal to ligand ratios in the preparation of the complexes. Excess ligand (ratio 1:≥2) renders the compounds $M(amtp)X_2(H_2O)_{0,1}$ (type I), while excess of metal salt (ratio ≥2:1) renders the compounds $M_3(amtp)_2X_6$ (type II).

For the cobalt type I chloride and thiocyanate, the ligand field spectrum is typical for five-coordination (distorted trigonal bipyramidal cobalt surroundings). The conductivity data (see 'Supplementary Material') suggest 1:1 electrolytes, while the ligand field spectra in nitromethane are very similar to the spectra in the solid state. Apparently only one of the anions is coordinated to the cobalt ion, while the other is not.

The conductivity data of the Ni, Cu and Zn type I chlorides and thiocyanates show them to behave as non-electrolytes, denoting that both anions are coordinated. This means that the metal ions are six-coordinated when all four donor N atoms of amtp take part in the coordination. The ligand field spectra (see Table 2) of the nickel compounds are indeed typical for an octahedral coordination geometry [14].

For the type II cobalt compounds the ligand field spectra are superpositions of the spectra of five-coordinated and four-coordinated cobalt(II). Together with the analytical data this points to the formula $[Co(amtp)X]_2[CoX_4]$. That the formula $[M(amtp)X]_2[MX_4]$ is the correct one for the Co, Cu and Zn type II compounds is further demonstrated by their infrared spectra, which indicate the presence of tetrahedral MX_4^{2-} anions [15], and from their conductivity data, which are in agreement with a 2:1 electrolyte. The related ligand tris(3,5-dimethyl-1-pyrazolylmethyl)amine (amtd) also forms type II compounds [4]. Type II compounds did not form with nickel, which is in accordance with the strong preference of Ni(II) for an octahedral coordination geometry.

With the nitrates only a cobalt and a zinc compound could be isolated with the ligand amtp (see Table 1). The ligand field spectrum of the cobalt compound indicates five-coordination, suggesting

TABLE 2. Ligand field absorption bands (cm^{-1}) and X-band EPR data of the amtp and am2p compounds

$Co(amtp)Cl_2(H_2O)$	6300abr, 11000, 17700sh, 19200		
$Ni(amtp)Cl_2(H_2O)$	9000, 12600w, 15600, 24900		
$Cu(amtp)Cl_2(H_2O)$	14300	$g_{\parallel} = 2.23$	$g_{\perp} = 2.07$ (A)
$Co(amtp)(NCS)_2$	6300abr, 12100, 17800		
$Ni(amtp)(NCS)_2$	10300, 12900(sh), 17300, 27000		
$Cu(amtp)(NCS)_2$	15200	$g_{\parallel} = 2.20$	$g_{\perp} = 2.09$ (A)
$Co(amtp)(NO_3)_2$	7000vbr, 12500, 19000		
$Co_3(amtp)_2Cl_6$	6100, 7500, 11400, 14700, 15700, 17400, 18900		
$Co_3(amtp)_2(NCS)_6$	7600abr, 12500, 16100, 17500sh, 19200sh		
$Cu_3(amtp)_2Cl_6$	7200avbr, 11500abr, 24400		
	$g_1 = 2.03$	$g_2 = 2.10$	$g_3 = 2.23$ (R)
$Ni(am2p)_2Cl_2$	11400, 12500sh, 18900, 28500		
$Co(am2p)_2(NO_3)_2$	10700, 18800sh, 20000sh, 21700		
$Ni(am2p)_2(NO_3)_2$	11400, 12500sh, 19000, 28500		
$Cu(am2p)Cl_2(H_2O)$	14500a	$g_{\parallel} = 2.22$	$g_{\perp} = 2.06$ (A)
$Cu(am2p)(NO_3)_2$	13900a	$g_{\parallel} = 2.20$	$g_{\perp} = 2.09$ (A)
$Cu(am2p)(pz)Cl_2(H_2O)_2$	14400	$g = 2.06$ (E)	
$Cu(am2p)(pz)(NO_3)_2(H_2O)$	15700	$g = 2.06$ (E)	
$Cu(am2p)(pz)(NCS)_2(H_2O)_2$	9300br, 13900	$g = 2.09$ (E)	

v = very, sh = shoulder, w = weak, br = broad, a = asymmetric; (A) = axial signal, no hyperfine splitting observed; (R) = rhombic signal; (E) = asymmetric exchange narrowed signal.

monodentate coordination of one nitrate ion. The infrared spectrum of the zinc compound is similar to that of the cobalt compound, however their X-ray patterns are different. The difference can be accounted for by the extra water molecule in the lattice of the zinc compound. Also, in solution, both compounds behave as 2:1 electrolytes [16], denoting one coordinating and one non-coordinating nitrate ion [17].

The am2p Compounds

With transition metal fluoroborates and nitrates, solid coordination compounds of tris(1-pyrazolylmethyl)amine (amtp) could hardly or not be obtained [7, 9]. Instead, compounds were obtained with the ligand bis(1-pyrazolylmethyl)amine (am2p). With Cu(II) compounds were also isolated with both am2p and pyrazole (pz) itself (see Table 1 and ref. 7). The ligands am2p and pz are hydrolysis products from amtp. Even with the transition metal salts of the coordinating anions Cl^- and NCS^- it was difficult to obtain amtp compounds. The origin of this phenomenon lies in the restricted coordination geometry which can be spanned by the four donor atoms of amtp. The N(amine)-to-N(pyrazole) bite of all pyrazole-substituted amine ligands spans an angle of about 80° [4–9, 17, 18], which is substantially smaller than the coordination angle of 90° or larger, needed for instance in octahedral, square pyramidal or trigonal pyramidal coordination. With amtp three such angles must be spanned simultaneously, which apparently gives too much strain in most cases. From the X-ray crystal structure of $Zn(amtp)(NCS)_2$ (which could not be isolated in large quantities, but a single crystal was obtained) it appeared even that in that case amtp only uses two pyrazole N atoms to coordinate, the third pyrazole N atom and the amine N atom do not participate in the coordination of the Zn(II) [6].

From the ligand field spectra of the Co(II) and Ni(II) am2p compounds (see Table 2) it is clear that the metal ions are octahedrally coordinated [14, 19, 20]. The crystal structure of $[Co(am2p)_2](NO_3)_2$ (see below) has confirmed that the CoN_6 chromophore is an almost regular octahedron.

The fact that the Cu(II) am2p compounds occur in two types (see Table 1) is not surprising in view of the large variety of coordination geometries encountered by Cu(II) [21]. Also, the chromophores (see Table 1) proposed for the Cu(II) compounds are less certain than those proposed for the Co(II) and Ni(II) compounds. In $[Cu(am2p)(pz)(BF_4)](BF_4)$, whose crystal structure has been described elsewhere [7], the Cu(II) ion is in a square pyramidal N_4F geometry, with the F atom of one of the anions in the apical position.

Description of the Structure of $[Co(am2p)_2](NO_3)_2$

The fractional coordinates of the non-hydrogen atoms are listed in Table 3. A PLUTO [22] projection is given in Fig. 1. Bond distances and bond angles of the non-hydrogen atoms are listed in

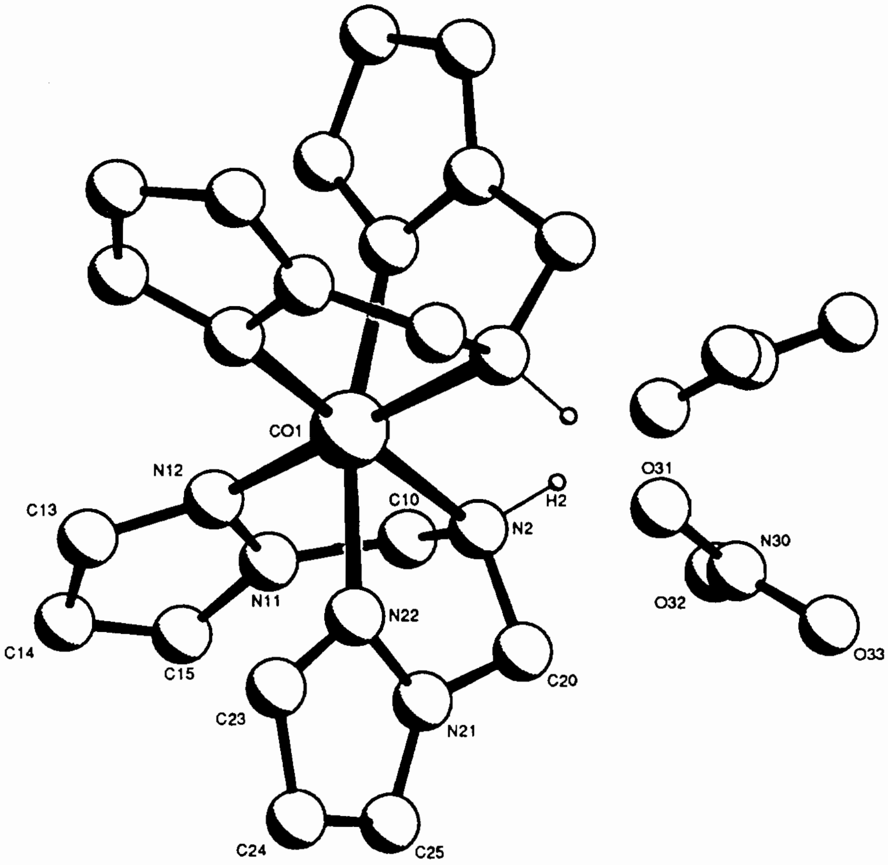

Fig. 1. PLUTO projection [22] and atomic labelling of the molecular entity $[Co(am2p)_2](NO_3)_2$. For clarity most hydrogen atoms are omitted.

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($Å^2 \times 10$) of the non-hydrogen atoms of $[Co(am2p)_2](NO_3)_2$

Atom	*x/a*	*y/b*	*z/c*	B_{eq} [a]
Co1	0	500	0	23
N2	568(2)	5132(2)	−1728(5)	26(1)
C10	983(2)	4947(3)	−896(8)	37(2)
N11	953(2)	5174(3)	776(6)	29(1)
N12	551(2)	5109(3)	1541(6)	31(1)
C13	628(2)	5355(3)	3019(6)	41(2)
C14	1079(2)	5553(4)	3172(7)	50(2)
C15	1272(2)	5434(3)	1732(7)	42(2)
C20	549(2)	5841(3)	−2407(6)	31(1)
N21	351(1)	6317(2)	−1221(5)	28(1)
N22	10(2)	6087(2)	−278(5)	29(1)
C23	−116(2)	6633(3)	610(7)	40(2)
C24	143(2)	7218(3)	200(11)	52(2)
C25	434(2)	6995(3)	−965(8)	42(2)
N30	−699(1)	6095(2)	−4865(6)	35(1)
O31	−990(2)	5961(3)	−3850(7)	85(2)
O32	−321(1)	5858(3)	−4624(7)	66(2)
O33	−810(1)	6440(2)	−6051(5)	47(1)

[a] $B_{eq} = 8/3 \cdot \pi^2$ trace *U*.

Table 4. See also 'Supplementary Material'. The cobalt ion is coordinated by four pyrazole nitrogens and two amine nitrogens of two symmetry related am2p ligands in a slightly distorted octahedral array. The am2p ligand chelates in the vicinal mode to the cobalt ion. The coordination angles spanned by the pyrazole N to amine N bites of the ligands range from 78.3° to 78.8°. Such restricted coordination angles have been encountered with all compounds of pyrazole-substituted amine ligands [4, 5, 17, 18]. The cobalt to pyrazole N distances are 2.088(5) and 2.087(4) Å, while the cobalt to amine N distance is 2.229(5) Å. These distances are comparable to metal to N distances in coordination compounds of related ligands [4, 5, 7]. The hydrogen atoms on the amine N atoms are weakly hydrogen bonded to the anions (see Table 4). There are no other intermolecular distances shorter than the van der Waals distances. The pyrazole rings are planar with distances to the least-squares planes of less than 0.02 Å and there is no stacking between the rings. So, the crystal packing is determined by the hydrogen bonding of the ligands to the anions and normal van der Waals contacts.

TABLE 4. Bond lengths (A) and bond angles (°) of $[Co(am2p)_2](NO_3)_2$

Co1–N2	2.229(5)	C20–N21	1.465(6)
Co1–N12	2.088(5)	N21–N22	1.353(6)
Co1–N22	2.087(4)	N21–C25	1.334(6)
N2–C10	1.454(8)	N22–C23	1.331(7)
N2–C20	1.467(6)	C23–C24	1.399(8)
C10–N11	1.463(8)	C24–C25	1.37(1)
N11–N12	1.358(7)	N30–O31	1.235(7)
N11–C15	1.333(8)	N30–O32	1.225(6)
N12–C13	1.339(7)	N30–O33	1.233(6)
C13–C14	1.395(9)	N2–H2	0.961
C14–C15	1.349(9)	O32–H2	2.212
N2–Co1–N12	78.3(2)	N11–C15–C14	107.2(5)
N2–Co1–N22	78.8(2)	N2–C20–N21	109.0(4)
N12–Co1–N22	87.6(2)	C20–N21–N22	119.4(4)
Co1–N2–C10	107.6(3)	C20–N21–C25	129.4(4)
Co1–N2–C20	109.0(3)	N22–N21–C25	111.0(4)
C10–N2–C20	116.1(4)	Co1–N22–N21	113.3(3)
C10–N2–H2	106.5(3)	Co1–N22–C23	135.3(4)
C20–N2–H2	104.3(3)	N21–N22–C23	106.3(4)
N2–C10–N11	109.4(5)	N22–C23–C24	109.5(5)
C10–N11–N12	118.3(5)	N22–C23–H23	125.1(3)
C10–N11–C15	129.7(5)	C24–C23–H23	125.3(4)
N12–N11–C15	112.0(5)	C23–C24–C25	105.7(5)
Co1–N12–N11	113.9(4)	N21–C25–C24	107.4(5)
Co1–N12–C13	137.3(4)	O31–N30–O32	116.7(5)
N11–N12–C13	104.6(5)	O31–N30–O33	118.3(5)
N12–C13–C14	110.1(5)	O32–N30–O33	125.0(5)
C13–C14–C15	106.2(5)		

Concluding Remarks

The present study has made clear that the ligand tris(pyrazol-1-ylmethyl)amine may act as a tetradentate ligand, coordinating through the amine nitrogen and the three pyrazole nitrogens. Six-coordination is observed for all nickel compounds, while five-coordination is observed for all amtp compounds with cobalt. The chlorides and thiocyanates of amtp form both $M(amtp)X_2$ (type I) and $[M(amtp)X]_2[MX_4]$ (type II) compounds, while tris(3,5-dimethyl-1-pyrazolylmethyl)amine (amtd) only forms type II compounds with cobalt, copper, and zinc. Apparently, the sterical hindrance of the methyl groups of amtd is such as to make the coordination of two anions in the complex cation (type I) unfavourable. Only with nickel(II), with its strong preference for an octahedral surrounding, is the type I complex the most stable form for both amtp or amtd. The presence of the methyl groups of amtd seems also a better protection against hydrolysis, as fewer bis(3,5-dimethylpyrazol-1-ylmethyl)amine (am2d) compounds [5] than am2p compounds were isolated.

Supplementary Material

Lists of the conductivity data and analytical data, of the atomic coordinates of the hydrogen atoms, of the non-hydrogen anisotropic thermal parameters, of the bond distances and bond angles, and of the observed and calculated structure factors are available from the authors on request.

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