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Mixed Acetato–Perchlorate Transition Metal Complexes of Pyrazole Substituted Ammonia. Crystal Structure of [(acetato)(aqua)(tris(3,5-dimethyl-1-pyrazolylmethyl)amine)cobalt(II)] Perchlorate

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Abstract

Mononuclear mixed anion (acetato–perchlorate) transition metal compounds with the ligand tris(3,5-dimethyl-1-pyrazolylmethyl)amine (amtd), of general formula [M(H_2O)(amtd)(OAc)](ClO_4), where M is Co (**1**) or Ni (**2**), and [M(amtd)(OAc)](ClO_4), where M is Co (**3**) or Cu (**4**), are described. In all compounds amtd acts as a chelating tetradentate ligand. Compounds **1** and **2** are isomorphous with an octahedral coordination geometry. Compounds **3** and **4** are isomorphous with five-coordinated metal ions. The ligand amtd has been hydrolyzed partly in forming the compound [Cu(H_2O)(am2d)(dmpz)(OAc)](ClO_4) (**5**), where am2d is bis(3,5-dimethyl-1-pyrazolylmethyl)amine and dmpz is 3,5-dimethylpyrazole.

The structure of **1** consists of a six-coordinate [Co(H_2O)(amtd)(OAc)] cation and a perchlorate anion. Space group $P2_12_12_1$ (orthorhombic) with a = 7.985(2), b = 16.833(2), c = 19.839(3) Å, Z = 4. The structure was solved by heavy-atom methods and refined by least-squares methods to a residual R of 0.044 (R_w = 0.048) for 1272 reflections. The Co(II) ion is octahedrally surrounded by the three nitrogens of the pyrazole groups with distances of 2.120(10), 2.138(9) and 2.159(9) Å and the amine nitrogen on 2.239(8) Å. The acetate anion and the water molecule occupy the fifth and the sixth coordination site, with cobalt to oxygen distances of 2.112(8) and 2.076(6) Å, respectively. The coordinated acetate anion is both intra- and inter-molecular hydrogen bonded to the hydrogen atoms of the coordinated water molecule, with 0 to 0 distances of 2.60(2) and 2.67(1) Å, thus forming infinite chains of cations.

Introduction

The coordination chemistry of polypyrazolyl ligands, *viz.* the uninegative poly(1-pyrazolyl)borates and the neutral poly(1-pyrazolyl)methanes, has developed rapidly in the last two decades [1, 2].

Recently, poly(1-pyrazolyl)amines have been introduced as a new branch of pyrazole-derived ligands [3]. These three types of polypyrazolyl ligands have similar configurations. However, apart from the pyrazole N atoms, which constitute the only donor atoms in the poly(1-pyrazolyl)borates and -methanes, the poly(1-pyrazolyl)amines also possess an amine N atom which may coordinate [4, 5]. Dinuclear carboxylato-bridged coordination compounds have been reported with the tris(1-pyrazolylborato) ligand [6, 7]. A similar coordination behavior of its configurational analog tris(3,5-dimethyl-1-pyrazolylmethyl)amine (amtd) with transition metal acetates seemed likely.

In the present paper we report the synthesis and spectroscopic characterization of several metal(II) acetato–perchlorate compounds of amtd and the X-ray crystal structure determination of the representative compound [Co(amtd)(H_2O)(OAc)](ClO_4).

Experimental

Starting Materials and Syntheses

The synthesis of the ligand tris(3,5-dimethyl-1-pyrazol-ylmethyl)amine was performed by a modification of the method reported by Driessen [3]. Equivalent amounts of *N*-(hydroxymethyl)-3,5-dimethylpyrazole (4.5 mmol) and of ammonium acetate (1.5 mmol) were stirred for 24 h at room temperature in 100 ml of CH_3CN. The organic solvent was removed under reduced pressure, rendering a colorless oil which, after treatment with 20 ml of water and cooling to 4 °C, yielded a white crystalline product. The compound was characterized by infrared and ^1H NMR spectra. ^1H NMR (DMSO) (ppm): 5.78(s, 3H, C4–H), 4.92(s, 6H, CH2), 2.15(s, 9H, CH3), 1.77(s, 9H, CH3). All other chemicals were commercially available, were of sufficient purity, and were used without further treatment.

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Caution. Perchlorate salts can be explosive and should be handled with care.

The compounds were prepared by adding dropwise 0.34 g (1 mmol) of the ligand amtd in ethanol (10 ml) to a stirred solution of 1 mmol of the appropriate hydrated metal perchlorate in 10 ml of ethanol, followed by addition of 0.7 g (5 mmol) of NaOAc·$3H_2O$ in 10 ml of water. The resulting reaction mixture was stirred for two hours. The single crystal of [(acetato)(aqua)(tris(3,5-dimethyl-1-pyrazolylmethyl)-amine)cobalt(II)]perchlorate (**1**) suitable for X-ray diffraction was obtained by slow evaporation of the solvent in the air. From the compound [Co(amtd)-(OAc)](ClO_4) (**3**) also a single crystal was isolated. However, the structure of **3** could only be refined to a final R value of 0.112 ($R_w = 0.147$) due to severe disorder. X-ray collection data on **3** are available, see 'Supplementary Material'.

Spectral and Magnetic Measurements

Infrared spectra (4000–180 cm^{-1}) were recorded on a Perkin-Elmer PE380 instrument, using KBr pellets, and/or nujol mulls between polyethene discs.

Solid state electronic spectra were measured, in the visible and near infrared (2000–300 nm), on a Perkin-Elmer UV330 Instrument in the diffuse reflectance mode with MgO as a reference.

EPR spectra were obtained on a Varian E-3 X-band spectrometer.

Proton NMR spectra (in DMSO-d_6 solutions) were recorded on the Jeol LNM PS100 instrument, operating at 99.5 MHz with TMS as an internal reference.

X-ray powder diffraction diagrams of the compounds were obtained with a Guinier-de Wolff camera.

Magnetic susceptibility measurements (80–300 K) were carried out with the Faraday method.

X-ray Methods and Structure Determination

A pink needle (0.6 × 0.3 × 0.1 mm) of [Co-$(C_{18}H_{27}N_7)(H_2O)(C_2H_3O_2)$]($ClO_4$), $M_r = 576.81$, 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 ω/θ mode. Orthorhombic space group $P2_12_12_1$. Cell dimensions from the setting angles of 24 reflections ($10° < \theta < 12°$): $a = 7.985(2)$, $b = 16.833(2)$, $c = 19.839(3)$ Å; $Z = 4$; $D_{calc} = 1.437$ g cm^{-1}; $F(000) = 1197.92$. Intensities were corrected for Lorentz polarization effects. No absorption correction was applied ($\mu = 7.911$ cm^{-1}, merging $R = 0.069$). 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; no significant changes in the intensities were observed. Ranges: $2.0° < \theta < 25°$, $-9 < h < 9$, $0 < k < 20$, $0 < l < 23$. A total of 2697 independent reflections were measured of which 1272 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 [8]. The atomic scattering factors were taken from ref. 9. The non-hydrogen atoms were refined anisotropically. The function minimized was $\Sigma w|F_o - F_c|^2$ with $w = 1/\sigma^2(F)$. The oxygen atoms of the perchlorate groups are disordered: constraint refinement was used with Cl–O distances of 1.41 Å and an O–Cl–O angle of 109.3°. 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 H atoms of the water molecule could not be located. The methyl H atoms and the non-methyl H atoms were assigned overall isotropic temperature factors giving final B values of 13.7 and 4.2 $Å^2$ respectively. At the final stage the conventional discrepancy index $R_F = \Sigma(|F_o - F_c|)/\Sigma F_o$ had been reduced to 0.044 and the weighted factor $R_w = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{1/2}$ to 0.048. Maximum positive and negative densities in the final difference Fourier are 0.35 and −0.30 e $Å^{-3}$ respectively. Estimated standard deviations were calculated with the use of a correlation matrix. The fractional coordinates of the non-hydrogen atoms are listed in Table I. See also 'Supplementary Material'.

Results and Discussion

General Considerations

In Table II the acetato–perchlorate compounds are listed with their colors, X-ray powder diffraction types and spectroscopic data. All compounds gave satisfactory elemental analyses. The compounds [M(H_2O)(amtd)(OAc)](ClO_4) where M is Co (**1**) or Ni (**2**) are isomorphous, and the compounds [M-(amtd)(OAc)](ClO_4) where M is Co (**3**) or Cu (**4**) are isomorphous. In the infrared spectra of all compounds strong absorption bands at about 1560 and about 1395 cm^{-1} are observed, which indicate the presence of monodentate coordinated acetate [10, 11]. Also a strong broad absorption band around 1100 cm^{-1} and a sharp band at 620 cm^{-1}, characteristic for ionic ClO_4^- [11], are observed in all compounds.

Description of the Structure of [Co(H_2O)(amtd)-(OAc)](ClO_4) (1)

An ORTEP [12] projection of **1** is given in Fig. 1. Selected bond distances and bond angles of the non-

TABLE I. Atomic Coordinates (Co(01), Cl(40) × 10^4, others × 10^3) and Equivalent Isotropic Thermal Parameters (Co(01) Å^2 × 10^2, others Å^2 × 10) of the Non-hydrogen Atoms of [Co(amtd)(H_2O)(OAc)](ClO_4) (1)

Atom	*x/a*	*y/b*	*z/c*	B_{eq}[a]
Co(01)	4638(2)	643(1)	392(1)	305(4)
N(02)	480(1)	−68(1)	32(1)	30(2)
O(03)	461(1)	187(1)	47(1)	42(2)
O(04)	718(1)	71(1)	10(1)	42(2)
O(05)	744(1)	197(1)	−17(1)	57(3)
C(06)	790(2)	126(1)	−20(1)	39(4)
C(07)	935(2)	105(1)	−62(1)	70(5)
C(10)	538(1)	−84(1)	−36(1)	34(3)
N(11)	455(1)	−34(1)	−83(1)	37(3)
N(12)	423(1)	43(1)	−66(1)	34(3)
C(13)	377(1)	77(1)	−124(1)	38(4)
C(14)	378(2)	24(1)	−175(1)	47(4)
C(15)	430(2)	−48(1)	−149(1)	43(4)
C(16)	341(2)	164(1)	−125(1)	55(4)
C(17)	457(2)	−126(1)	−182(1)	67(5)
C(20)	311(1)	−100(1)	41(1)	35(3)
N(21)	210(1)	−49(1)	86(1)	35(3)
N(22)	222(1)	32(1)	74(1)	39(3)
C(23)	100(1)	61(1)	113(1)	34(3)
C(24)	12(1)	3(1)	146(1)	40(3)
C(25)	84(1)	−67(1)	128(1)	38(3)
C(26)	73(2)	150(1)	117(1)	52(4)
C(27)	47(2)	−150(1)	146(1)	56(4)
C(30)	596(1)	−92(1)	86(1)	36(3)
N(31)	566(1)	−46(1)	145(1)	34(3)
N(32)	553(1)	34(1)	139(1)	36(3)
C(33)	546(2)	63(1)	201(1)	40(3)
C(34)	562(2)	1(1)	248(1)	49(4)
C(35)	574(1)	−68(1)	210(1)	41(4)
C(36)	528(2)	150(1)	213(1)	57(4)
C(37)	590(2)	−152(1)	233(1)	58(5)
Cl(40)	5274(5)	1760(2)	4220(2)	49(1)
O(41A)	533(5)	96(1)	440(1)	94(9)
O(42A)	376(3)	193(2)	387(2)	104(9)
O(43A)	531(5)	223(1)	481(1)	102(9)
O(44A)	664(3)	197(2)	381(2)	81(6)
O(41B)	522(5)	98(1)	398(1)	110(9)
O(42B)	366(2)	211(2)	416(2)	90(9)
O(43B)	575(4)	177(1)	490(1)	95(9)
O(44B)	641(3)	222(2)	384(1)	68(6)

[a] B_{eq} = 8/3 × π^2 trace *U*.

hydrogen atoms are listed in Table III. The cobalt ion is in a six-coordinate environment formed by three pyrazole nitrogens and by the amine nitrogen atom of the amtd ligand, by one oxygen atom of the acetate ion and by the oxygen of the water molecule. The coordination geometry is approximately octahedral with the amine nitrogen and the water oxygen in the axial positions. The Co–N and Co–O bond lengths are comparable to those in two related Co(II)/amtd compounds, with the Co–O(03) distance of 2.076(6) Å slightly but significantly longer [5, 13].

TABLE II. X-ray Powder Diffraction and Infrared Types, Colours and Spectroscopic Data (Ligand Field, X-band EPR, Magnetic Moments) of the Acetato–Perchlorate Compounds

Compound	Colour	X-ray type[a]	IR type[b]	Ligand field (cm^{-1})	*Dq*[c]	*B*[c]	μ_{eff} (BM) (295 K)
1 [Co(H_2O)(amtd)(OAc)](ClO_4)	pink	A	I	8770(br), 20200	960	840	4.75
2 [Ni(H_2O)(amtd)(OAc)](ClO_4)	light blue	A	I	9700(br), 12900(w), 16130, 26000	970	870	3.11
3 [Co(amtd)(OAc)](ClO_4)	violet	B	II	7140, 13900, 20200			4.32
4 [Cu(amtd)(OAc)](ClO_4)	green	B	II′	11760[d]	g_{iso} = 2.10[e]		
5 [Cu(H_2O)(am2d)(dmpz)(OAc)](ClO_4)	blue	C	III	13900[f]	g_{iso} = 2.10[e]		

[a] The same letters indicate identical X-ray powder patterns. [b] The same roman numerals indicate very similar infrared spectra. [c] Values in cm^{-1} (br = broad, w = weak). [d] Broad asymmetric. [e] Isotropic signals (X-band EPR) at room temperature and at liquid nitrogen. [f] Distinct shoulder at the low energy side.

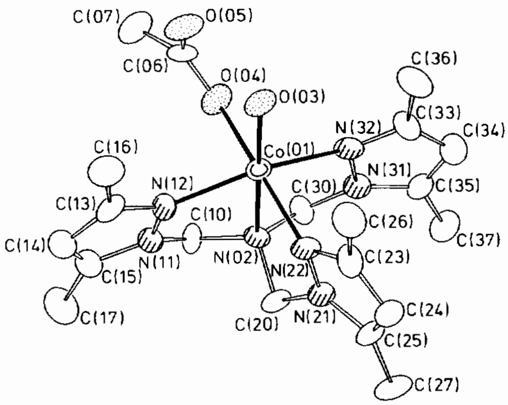

Fig. 1. ORTEP [12] projection and atomic labeling of [Co(H_2O)(amtd)(OAc)](ClO_4). For clarity the perchlorate anion and the hydrogen atoms are omitted.

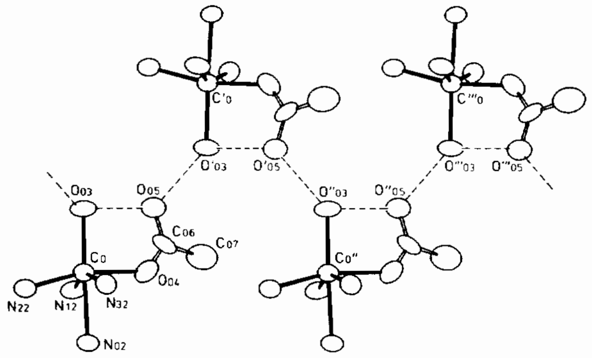

Fig. 2. The acetate–water hydrogen bond chain structure in the (100) direction of [Co(H_2O)(amtd)(OAc)](ClO_4). Symmetry operation code: $(') = \frac{1}{2} + x, \frac{1}{2} - y, -z$; $('') = 1 + x, y, z$; $(''') = \frac{3}{2} + x, \frac{1}{2} - y, -z$.

The O(03)...O(05) distances indicate that hydrogen bonding occurs between the coordinated water molecule and the acetate ion. The water H atoms, which could not be located, are assumed to be in between the O atoms. The hydrogen bonding pattern is depicted in Fig. 2, showing chains of O–H...O contacts in the (100) direction. O–O distances are 2.60(1) Å for the intramolecular O(03)...O(05) contact, and 2.67(1) Å for the intermolecular O(05)...O'(03) contact. The strong hydrogen bonds are also reflected by the infrared spectra. The pyrazole rings are planar with distances to the least-squares planes of less than 0.01 Å. No stacking of the pyrazole rings occurs. The crystal packing is determined by hydrogen bonding and van der Waals contacts.

TABLE III. Selected Bond Lengths (Å) and Bond Angles (°) of the Non-hydrogen Atoms of [Co(amtd)(H_2O)(OAc)](ClO_4) (1)

Co(01)–N(02)	2.239(8)	N(02)–Co(01)–O(03)	177.2(3)
Co(01)–O(03)	2.076(6)	N(02)–Co(01)–O(04)	88.9(3)
Co(01)–O(04)	2.112(8)	N(02)–Co(01)–N(12)	77.3(3)
Co(01)–N(12)	2.138(9)	N(02)–Co(01)–N(22)	79.6(3)
Co(01)–N(22)	2.12(1)	N(02)–Co(01)–N(32)	78.8(3)
Co(01)–N(32)	2.159(9)	O(03)–Co(01)–O(04)	88.7(3)
N(02)–C(10)	1.44(1)	O(03)–Co(01)–N(12)	103.8(3)
N(02)–C(20)	1.47(1)	O(03)–Co(01)–N(22)	102.8(4)
N(02)–C(30)	1.47(1)	O(03)–Co(01)–N(32)	99.7(3)
O(04)–C(06)	1.23(1)	O(04)–Co(01)–N(12)	83.3(3)
O(05)–C(06)	1.26(1)	O(04)–Co(01)–N(22)	167.7(3)
C(06)–C(07)	1.46(2)	O(04)–Co(01)–N(32)	87.2(3)
C(10)–N(11)	1.43(1)	N(12)–Co(01)–N(22)	98.1(3)
N(11)–N(12)	1.37(1)	N(12)–Co(01)–N(32)	154.4(3)
C(20)–N(21)	1.47(1)	N(22)–Co(01)–N(32)	86.4(4)
N(21)–N(22)	1.38(1)	Co(01)–N(02)–C(10)	105.6(6)
C(30)–N(31)	1.43(1)	Co(01)–N(02)–C(20)	107.6(6)
N(31)–N(32)	1.35(1)	Co(01)–N(02)–C(30)	104.8(6)
		Co(01)–O(04)–C(06)	128.7(8)
O(03)–O(05)	2.60(1)	Co(01)–N(12)–N(11)	111.8(7)
O(03)–O'(05)	2.67(1)	Co(01)–N(12)–C(13)	144.3(8)
		Co(01)–N(22)–N(21)	111.7(7)
		Co(01)–N(22)–C(23)	139.3(8)
		Co(01)–N(32)–N(31)	110.1(7)
		Co(01)–N(32)–C(33)	138.4(7)
		O(04)–C(06)–O(05)	123(1)
		O(04)–C(06)–C(07)	118(1)
		O(05)–C(06)–C(07)	119(1)

(') Symmetry operation $(x - \frac{1}{2}, -y + \frac{1}{2}, -z)$.

Spectroscopic Properties

The ligand field spectra of **1** and **2** are typical for six-coordinate Co(II) and Ni(II) [14, 15], consistent with the X-ray structure of **1**. The rather high values of the ligand field Racah parameter *B* for the compounds **1** and **2**, see Table II, indicate distorted octahedral coordination geometries for cobalt(II) and nickel(II), while the values for *Dq* are consistent with a mixed donor atom (N_4O_2) chromophore [16].

The ligand field spectrum of [Co(amtd)(OAc)]-(ClO_4) (**3**) is typical for five-coordinated cobalt(II) ions [17]. From the partly resolved structure (see above) of this Co(II) compound it was clear that three pyrazole nitrogens, the amine nitrogen and one oxygen of the acetate ion are coordinated to the cobalt ion. The coordination geometry is approximately trigonal bipyramidal with amtd in a tripodal coordination mode.

Magnetic measurements in the region 80–300 K for the compounds **1**, **2** and **3** show a monotonous increase in the susceptibility with decreasing temperature, as expected for non-coupled monomeric metal ions in the high-spin state. This means that the intermolecular hydrogen bond between the six-coordinated cobalt(II) species is not an efficient enough exchange pathway to effect any measurable coupling. Room temperature magnetic moments are listed in Table II. The room temperature magnetic moment of the five-coordinate Co(II) compound is smaller than the magnetic moment of the six-coordinated Co(II) compound in agreement with reported values [5, 13, 17].

For the copper(II) compound (**4**) the ligand field spectrum is consistent with five-coordinated Cu(II) (Table II). Compound **5** is remarkable as it contains both bis(3,5-dimethyl-1-pyrazolylmethyl)amine (am2d) and 3,5-dimethylpyrazole (dmpz) formed through the partial hydrolysis of amtd. So far, with amtd such compounds have not been isolated [5, 18]. With the ligand tris(1-pyrazolylmethyl)amine (amtp), which is different from amtd only in not bearing ring substituents, such compounds with partial hydrolysed amtp have been reported [19, 20]. The ligand field spectrum of **6** indicates a six-coordinate copper(II) geometry. Both Cu(II) compounds showed an isotropic EPR signal (see Table II), indicative for exchange-narrowed signals, caused by the fact that the Cu ions are too close to each other in the crystal lattice.

In conclusion, we have shown that mononuclear coordination compounds are formed when the tripodal tetradentate N-donor ligand tris(3,5-dimethyl-1-pyrazolylmethyl)amine is reacted with transition metal ions in the presence of the acetate ion.

Supplementary Material

The following are available on request from the authors: Table Suppl. 1: Bond lengths of [Co(H_2O)(amtd)(OAc)](ClO_4) (**1**) (1 page); Table Suppl. 2: Bond angles of **1** (2 pages); Table Suppl. 3: Fractional coordinates of the hydrogen atoms of **1** (1 page); Table Suppl. 4: Anisotropic thermal parameters of the non-hydrogen atoms of **1** (1 page); Table Suppl. 5: List of structure factors of **1** (4 pages); Table Suppl. 6: Analytical data (1 page); Table Suppl. 7: X-ray collection data for [Co(amtd)(OAc)](ClO_4) (**3**) (1 page).

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