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A Co(III) complex of carbonic anhydrase inhibitor methazolamide and the amino-imino 'aib' ligand formed by reaction of acetone and ammonia

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Abstract

Reaction of $Co(NO_3)_2 \cdot 6H_2O$ with methazolamide {[*N*-(3-methyl-5-sulfamoyl-1,3,4-thiadiazol-2(3*H*)-ylidene)acetamide] (Hmacm)} and ammonia in acetone to produce $[Co(methazolamidate)(2\text{-methyl-2-amino-4-iminopentane})_2(NH_3)](NO_3)_2 \cdot 2H_2O$ is described. The ligand 2-methyl-2-amino-4-iminopentane (aib) is the product obtained from the condensation of two ammonia and two acetone molecules. The complex crystallizes in the monoclinic space group $P2_1/c$ with $a = 16.713(5)$, $b = 9.180(1)$, $c = 20.273(1)$ Å, $\beta = 97.44(4)°$ for $Z = 4$. The R value is 0.081 for 2150 significant reflections. The Co(III) ion exhibits a nearly regular octahedral arrangement with the Co–N bond distances in the range 1.91–1.98 Å. The Co(III) ion is obtained by spontaneous oxidation of Co(II). Methazolamide interacts as a monodentate ligand through the deprotonated sulfonamido N atom in a similar way to the bonding of the inhibitor in the carbonic anhydrase enzyme.

Introduction

Unsubstituted sulfonamides are inhibitors of the Zn metallo-enzyme carbonic anhydrase (CA). These molecules bind to the active site of CA forming an inner ligand with Zn by displacing the water molecule ligand. The specific and tight binding has been shown to be dependent on both interaction between the inhibitor and Zn and the inhibitor and the protein. While Zn(II) is found in the native enzyme, Co(II) can be substituted with only a 50% reduction in the catalytic activity and no detectable change in the enzyme structure [1].

Only the sulfonamide type of inhibitors have been found to be useful clinically, because they are highly potent, selective and reversible.

Theoretical studies and X-ray diffraction data of the acetazolamide–HCAI complex have indicated that the deprotonated sulfonamido group is the unit that links the metal ion in the active site of the enzyme [2, 3].

Lack of research on the coordination chemistry of sulfonamides has focused our interest on the study of the ligand behaviour of acetazolamide [5-acetamide-1,3,4-thiadiazol-2-sulfonamide] (H_2acm) towards several divalent metal ions in order to discover the factors that make the binding of the inhibitor dependent on the metal. Although, in the first model complex, $Zn(Hacm)_2(NH_3)_2$ [4, 5], the drug acts as a monodentate ligand though the deprotonated sulfonamido N atom, the molecular structures of one Ni(II) and some Cu(II) complexes [6–8] have indicated a remarkable influence of the deprotonation of the ligand and its way of coordination. In fact, depending on the mode of deprotonation not only the sulfonamido N atom interacts with the metal ion, but also the thiadiazole N atoms and even the sulfonamido O one. Due to this singular coordination behaviour we have chosen, as a continuation of our investigation, an N-methyl derivative of H_2acm, methazolamide, Fig. 1. Substitution on the N

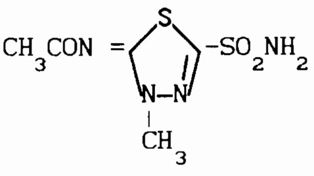

Fig. 1. Methazolamide.

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thiadiazole atom closest to the acetamido group modifies the coordination possibilities preventing the interaction via the N atoms of the ring. Up to now, as expected and as it occurs in the native enzyme, methazolamide has a strong preference to coordinate through the N atom of the sulfonamido group. In all the cases, the divalent complexes were isolated after the addition of ammonia or pyridine [9, 10]. The determination of the crystal structure of $[Co(macm)(aib)_2(NH_3)](NO_3)_2 \cdot 2H_2O$ reported here should allow us to obtain information concerning the influence of a trivalent metal ion on the geometry of the ligand. In addition a study of the reaction that leads to the formation of the amino-imino ligand aib, Fig. 2, was undertaken.

Experimental

Synthesis of the complex

Hmacm (5 mmol) was dissolved in acetone (100 ml) at 50 °C. Then, after heating at 80 °C, 1 mmol of $Co(NO_3)_2 \cdot 6H_2O$ was added with stirring. The resulting pink mixture was cooled to 50 °C and then 0.5 ml of concentrated ammonia was added dropwise with continuous stirring. Immediately on addition of the first drop of NH_3 a violet product was observed that turned into dark blue, then olive green and finally orange. After the addition of 0.5 ml of ammonia, the reaction mixture was left to stand at room temperature. On cooling, the solution colour changed from dark to light orange. Within a few days (2–3) prismatic orange crystals of $[Co(macm)(aib)_2(NH_3)](NO_3)_2 \cdot 2H_2O$ (**I**) were obtained and a small quantity of the orange solid **II** remained. The crystals were separated, washed and kept in a vacuum desiccator over silica gel. *Anal.* Found: C, 29.6; H, 5.9; N, 22.2; S, 9.1. Calc. for $CoC_{17}H_{43}N_{11}S_2O_{11}$: C, 29.1; H, 6.1; N, 21.9; S, 9.1%.

The orange solid **II** has been identified from the elemental analysis as $[Co(aib)_2(NH_3)_2](NO_3)_3 \cdot 2H_2O$. *Anal.* Found: C, 27.0; H, 6.7; N, 23.9. Calc. for $CoC_{12}H_{34}N_9O_{11}$: C, 26.8; H, 6.3; N, 23.4%.

Analyses

Elemental C, H, N and S analyses were performed by the microanalytical laboratory of the C.S.I.C. of Barcelona.

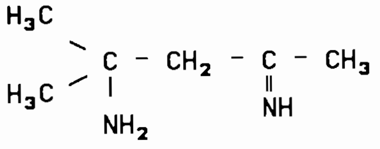


Fig. 2. aib.

Spectroscopic measurements

IR spectra in the range 4000–200 cm^{-1} of the sample pelleted in KBr were recorded on a Perkin-Elmer 843 spectrophotometer. Solid state electronic spectra (900–180 nm) were obtained on a Perkin-Elmer Lambda 15 spectrophotometer.

General considerations

The reaction of Hmacm, $Co(NO_3)_2 \cdot 6H_2O$ and concentrated aqueous ammonia in acetone medium gives rise to an unexpected diamagnetic Co(III)–methazolamidate complex (**I**) whose crystal structure reveals the presence of 2-methyl-2-amino-4-iminopentane, known as aib, Fig. 2, acting as a bidentate ligand. Together with the crystals of **I** a small quantity of an orange solid **II** was obtained. Analysis of **II** indicated a composition incorporating the aib ligand. From these data the solid **II** was identified as $[Co(aib)_2(NH_3)_2](NO_3)_3 \cdot 2H_2O$. During the synthesis process two facts that, of note, take place: first, the formation of the amino-imino aib, as a result of the condensation reaction of two acetone and two ammonia molecules in a template type reaction described by Curtis [11] and second, the air spontaneous oxidation of Co(II) to Co(III). In this sense the intermediate colour changes which occur in the reaction process suggest the possible involvement of Co(III) intermediate species (see Scheme 1), since it is known, oxidation of solutions of Co(II) salts and aqueous ammonia can give a number of cobaltammines [12].

To characterize the different steps of the synthesis described above and to understand the factors that control it we have made several attempts to vary the reaction conditions.

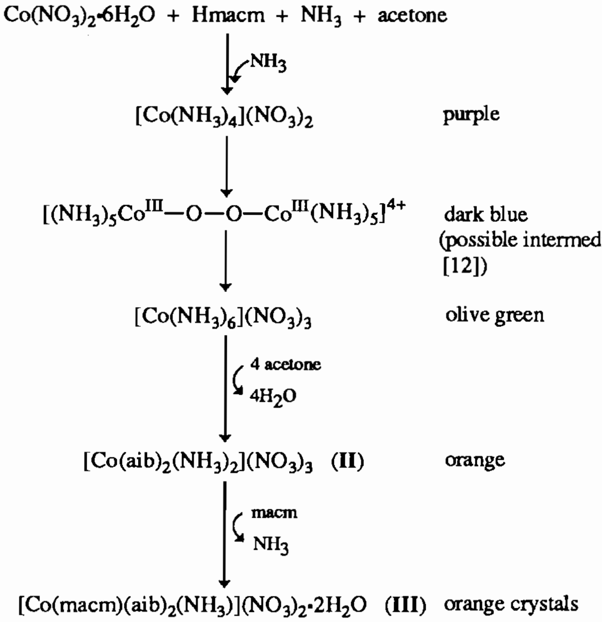
Following the synthesis method but in the absence of Hmacm an orange solid was obtained. From elemental analysis and IR spectral data this solid was assumed to be **II**. This fact seems to indicate that the methazolamide ligand substitutes one molecule of NH_3 in the coordination sphere of Co(III) in compound **II** to give compound **I**.

Under the same reaction conditions as those in the initial synthesis but with an excess of ammonia, a violet Co(II) complex **III** was formed. The solid **III** which previously was also obtained from an ethanolic solution of $CoCl_2 \cdot 2H_2O$, Hmacm and ammonia [13] corresponds to the $Co(macm)_2(NH_3)_2$ complex. Attempts performed with an aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ lead to the solid **III**; as expected the orange compound **II** is not formed.

The importance of the NO_3^- anion in the formation of the amino-imino aib was inferred using $CoCl_2 \cdot 2H_2O$ and $Co(ClO_4)_2 \cdot 6H_2O$ instead of the nitrate salt. Repeated attempts were unsuccessful, since no solids were obtained. This fact seems to indicate that suitable crystals of $[Co(macm)(aib)_2(NH_3)](NO_3)_2 \cdot 2H_2O$ are presumably formed because of the stabilization derived from the intricate hydrogen bond network that involves the nitrate anions, the aib and the water molecules. This can also be related to the instability of aib [14] which is stabilized by complex formation and by hydrogen bonds.

Due to the instability of aib we have also made attempts to isolate the diammine using perchloric acid [11] both in presence of Co(II) ion and in absence of it. In both cases the only product obtained was identified as ammonium perchlorate.

According to this evidence we propose the following sequence of reactions in the synthesis process



Scheme 1.

Crystallographic data collection and structure refinement

An orange-colored prismatic crystal of approximate dimensions 0.2×0.1×0.3 mm was mounted on a glass fiber and used for data collection on a CAD4 Enraf-Nonius four-circle automatic diffractometer. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 25 reflections in the range 7–14°. The monoclinic space group $P2_1/c$ was assumed due to the extinctions observed. Data were collected at 293 K using Mo Kα radiation ($\lambda = 0.71073$ Å) and the ω/θ scan technique. The data were corrected for Lorentz and polarization effects and empirical absorption correction [15] and a secondary extinction correction was applied [16]. The final coefficient refined in the last least-squares cycle was $1.89(1) \times 10^{-9}$.

The structure was solved by direct methods [17] which revealed the position of cobalt and twenty non-hydrogen atoms. The remaining non-hydrogen atoms were located from successive Fourier syntheses. All non-hydrogen atoms with the exception of the carbons of the 2-methyl-4-amino-2-pentamine ligands, nitrogen and oxygen of the nitrate groups, and oxygen of water molecules were refined anisotropically. The remaining atoms were refined isotropically. Hydrogen atoms were located from geometrical considerations, and added to the structure factor calculations as fixed contributions and their positional parameters were not refined. The structure was refined using full-matrix least-squares [18]. The refinement was complicated by the presence of statistical disorder in the nitrate ions and in the water molecules and in the high level of thermal motion in the crystal. The final R value was 0.081, with $R_w = 0.084$ (weighting scheme $w^{-1} = \sigma^2(F)$; 270 parameters; $S = 4.1$; maximum, Δ/σ in final cycle 0.001; maximum $\Delta\rho = 0.67$ e Å^3). Computations were performed on a DECMicroVAXII computer.

Final fractional coordinates for non-hydrogen atoms are given in Table 1. Crystal data and additional details of the data collection and refinement of the structure are presented in Table 2.

Results and discussion

Description of the structure $[Co(macm)(aib)_2(NH_3)](NO_3)_2 \cdot 2H_2O$

An ORTEP drawing of the complex, showing the atomic numbering scheme, is given in Fig. 3. Selected bond lengths and angles are given in Tables 3 and 4, respectively.

The structure is built up of four crystallographically independent $[Co(macm)(aib)_2(NH_3)]^{2+}$ units and nitrate ions which are hydrogen bonded to uncoordinated water molecules and to the N atoms of the aib ligands contributing to the overall crystalline stability.

The Co(III) ion exhibits a nearly regular octahedral geometry with a $CoNN'N''_2N'''_2$ chromophore. The basal plane is formed by four N atoms, N(12) amino and N(14) imino corresponding to one aib molecule, ammonia N(5) and N(22) amino from the other aib molecule. The axial positions are occupied by N(24) imino atom of the latter aib ligand and N(4) atom of the deprotonated sulfonamido group of methazolamide at similar distances to the equatorial ones. The Co–N(imino) and Co–N(amino) bond distances are consistent with the values reported for Co(III) complexes [19, 20]. As expected, the Co–N(amino) (1.97(2) Å) bond is longer than the Co–N(imino) (1.92(1) Å) bond. The difference in the Co–N(sulfonamido) distance in this complex compared to that in the previously

TABLE 1. Atomic coordinates for the [Co(macm)(aib)$_2$(NH$_3$)](NO$_3$)$_2$·2H$_2$O complex

Atom	x	y	z
Co	0.2187(1)	0.1015(2)	0.14267(8)
S(1)	0.2559(2)	−0.0765(4)	0.0119(2)
S(2)	0.3421(2)	0.8690(4)	0.5375(2)
O(1)	0.2068(5)	−0.169(1)	−0.0340(5)
O(2)	0.2830(6)	0.059(1)	−0.0109(4)
O(3)	0.3877(5)	0.334(2)	0.0598(5)
N(1)	0.4150(6)	−0.122(1)	0.0471(5)
N(2)	0.4710(6)	−0.228(1)	0.0631(5)
N(3)	0.4946(6)	−0.475(1)	0.0806(5)
N(4)	0.2164(6)	−0.056(1)	0.0768(5)
N(5)	0.3361(6)	0.128(1)	0.1444(5)
N(12)	0.0349(7)	0.252(2)	0.0734(5)
N(14)	0.1047(6)	0.079(1)	0.1413(5)
N(22)	0.2380(6)	−0.053(1)	0.2111(5)
N(24)	0.2175(7)	0.248(1)	0.2105(6)
C(1)	0.3461(7)	−0.178(1)	0.0324(6)
C(2)	0.4453(7)	−0.367(1)	0.0630(6)
C(3)	0.4606(8)	−0.610(2)	0.0788(6)
C(4)	0.5170(8)	−0.732(2)	0.1007(7)
C(5)	0.5558(8)	−0.180(2)	0.0825(8)
C(11)	0.134(1)	0.447839	0.006(1)
C(12)	0.123(1)	0.300(2)	0.0411(8)
C(13)	0.067(1)	0.313(2)	0.0937(9)
C(14)	0.0491(9)	0.174(2)	0.1230(8)
C(15)	−0.035(1)	0.144(2)	0.136(1)
C(16)	0.090(1)	0.189(2)	−0.011(1)
C(21)	0.325(1)	0.028(2)	0.3114(8)
C(22)	0.2418(8)	−0.024(2)	0.2840(7)
C(23)	0.179(1)	0.086(2)	0.2957(8)
C(24)	0.198(1)	0.228(2)	0.2698(8)
C(25)	0.201(1)	0.370(3)	0.311(1)
C(26)	0.225(1)	−0.168(2)	0.3169(9)
Nitrate anions			
N(30)	−0.056(1)	0.216(2)	0.326(1)
O(31)	−0.033(1)	0.317(2)	0.2998(9)
O(32)	−0.020(1)	0.101(2)	0.3250(9)
O(33)	−0.1138(9)	0.225(2)	0.3562(8)
N(40)	0.399(1)	0.494(3)	0.233(1)
O(41)	0.347(1)	0.548(3)	0.206(1)
O(42)	0.4072(9)	0.351(2)	0.2397(7)
O(43)	0.470(1)	0.543(2)	0.258(1)
Solvent			
O(4)	0.5957(9)	0.334(2)	0.3014(7)
O(5)	0.227(1)	0.552(3)	0.159(1)

reported [Co(macm)$_2$(py)$_2$(OH$_2$)$_2$] [10], 0.138 Å, corresponds well to octahedral covalent radii of Co(II) and Co(III) [21]. The four basal N atoms are almost coplanar. The Co(III) ion lies 0.006 Å below this plane. The distortion from octahedral symmetry is not very large considering that the relevant angles lie between 86.3 and 92.4°. This slight deviation from the ideal angles could arise from the constrained geometry of the chelating aib ligand and the hydrogen bonding network.

TABLE 2. Crystallographic data for the [Co(macm)(aib)$_2$(NH$_3$)](NO$_3$)$_2$·2H$_2$O complex

Chemical formula	$C_{17}H_{43}CoN_{11}O_{11}S_2$
Formula weight	701.67
Crystal class	monoclinic
Space group	$P2_1/c$
a (Å)	16.713(5)
b (Å)	9.713(2)
c (Å)	20.273(1)
β (°)	94.44(4)
V (Å^3)	3084.0
Z	4
λ(Mo Kα) (Å)	0.71073
ρ (g cm^{-3})	1.51
μ (cm^{-1})	7.50
F(000)	1480
Absorption correction: min.–max.	0.74–1.14
Max. (sin θ)/λ	0.616
Total no. reflections measured	6674
θ range (°)	3–26
No. unique reflections (R_{int})	6674
No. observed reflections (criterion)	2150($I > 3\sigma(I)$)
R	0.081
R_w	0.084

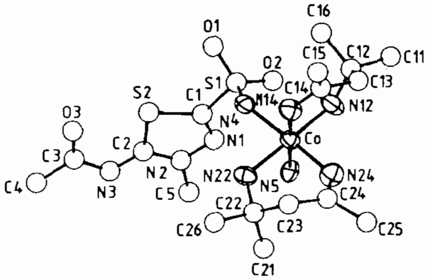


Fig. 3. ORTEP drawing of the [Co(macm)(aib)$_2$(NH$_3$)](NO$_3$)$_2$·2H$_2$O complex.

The crystal structure shows the aibs in *cis* position, however, *cis* and *trans* arrangements are possible for both diacetone-amino-imino ligands in the coordination polyhedron. This array could be favoured by means of hydrogen bonds between the equatorial ammonia molecule and the oxygen atom of the methazolamidate acetamido group.

The aib ligands act in a bidentate fashion achieving two six-membered chelated rings with the gauche conformation. Both aib molecules coordinate through their N amino atoms in *trans* positions to each other. Apparently, the steric hindrance of the methyl groups is such as to make the coordination of the two aib N amino atoms in a *trans* position favourable. Bond distances and angles in the amino-imino unit are within the range observed for comparable amino-imino complexes [20].

Concerning methazolamide, a comparison of the bond distances and angles in the SO$_2$NH$_2$ moiety of the present structure with those of methazolamide [22] and several of its complexes (Table 5) seems to point out that the shortening of the S–N bond distance is a result of the deprotonation and coordination of the ligand via the sulfonamido N atom but that it also depends on the nature of the metal ion. In fact the minor S–N bond length reduction in the Co(III)–macm complex with respect to the M(II)–macm complexes could be related to the trivalent character of the metal centre. The acetamido and thiadiazole units have a pattern similar to that observed in the uncoordinated methazolamide which is in accord to the lack of interaction of these groups with the metal ion.

TABLE 3. Bond distances (Å) for the $[Co(macm)(aib)_2(NH_3)](NO_3)_2 \cdot 2H_2O$ complex

Co–N(4)	1.97(2)	Co–N(14)	1.91(1)
Co–N(5)	1.97(1)	Co–N(22)	1.98(2)
Co–N(12)	1.97(1)	Co–N(24)	1.93(1)
S(1)–O(1)	1.44(1)	N(12)–C(12)	1.51(2)
S(1)–O(2)	1.42(2)	N(14)–C(14)	1.30(2)
S(1)–N(4)	1.56(2)	N(22)–C(22)	1.50(2)
S(1)–C(1)	1.78(1)	N(24)–C(24)	1.30(3)
S(2)–C(1)	1.76(1)	C(11)–C(12)	1.55(3)
S(2)–C(2)	1.74(1)	C(12)–C(13)	1.50(3)
N(1)–N(2)	1.36(1)	C(12)–C(16)	1.52(3)
N(1)–C(1)	1.26(2)	C(13)–C(14)	1.46(3)
N(2)–C(2)	1.35(2)	C(14)–C(15)	1.48(3)
N(2)–C(5)	1.49(2)	C(21)–C(22)	1.51(2)
N(3)–C(2)	1.32(2)	C(22)–C(23)	1.50(2)
N(3)–C(3)	1.36(2)	C(22)–C(26)	1.52(3)
C(3)–C(4)	1.50(2)	C(23)–C(24)	1.47(3)
O(3)–C(3)	1.24(1)	C(24)–C(25)	1.55(3)
O(31)–N(30)	1.17(3)	O(41)–N(40)	1.10(3)
O(32)–N(30)	1.21(3)	O(42)–N(40)	1.33(4)
O(33)–N(30)	1.20(3)	O(43)–N(40)	1.31(3)

TABLE 4. Bond angles (°) for the $[Co(macm)(aib)_2(NH_3)](NO_3)_2 \cdot 2H_2O$ complex

N(4)–Co–N(5)	92.0(4)	N(5)–Co–N(12)	87.2(4)
N(4)–Co–N(12)	92.4(5)	N(5)–Co–N(14)	179.1(4)
N(4)–Co–N(14)	88.7(4)	N(5)–Co–N(22)	90.3(4)
N(4)–Co–N(22)	86.3(4)	N(5)–Co–N(24)	90.2(5)
N(4)–Co–N(24)	176.5(5)	N(14)–Co–N(22)	90.2(4)
N(12)–Co–N(14)	92.4(5)	N(14)–Co–N(24)	89.2(5)
N(12)–Co–N(22)	177.1(5)	N(22)–Co–N(24)	91.5(5)
N(12)–Co–N(24)	90.4(5)		
O(1)–S(1)–O(2)	119.1(6)	C(1)–S(2)–C(2)	87.9(6)
O(1)–S(1)–N(4)	110.4(6)	N(2)–N(1)–C(1)	110.0(2)
O(1)–S(1)–C(1)	103.7(6)	N(1)–N(2)–C(2)	118.0(1)
O(2)–S(1)–N(4)	110.4(6)	N(1)–N(2)–C(5)	117.0(2)
O(2)–S(1)–C(1)	103.9(6)	C(2)–N(2)–C(5)	126.0(2)
N(4)–S(1)–C(1)	107.8(6)	C(2)–N(3)–C(3)	116.0(2)
S(1)–C(1)–N(1)	125.0(2)	O(3)–C(3)–C(4)	122.0(1)
S(2)–C(1)–N(2)	115.9(9)	N(3)–C(3)–C(4)	115.0(2)
S(2)–C(2)–N(2)	108.3(9)	O(3)–C(3)–N(3)	122.0(1)
S(2)–C(2)–N(3)	130.0(2)		
O(31)–N(30)–O(32)	120.0(2)	O(41)–N(40)–O(42)	124.0(2)
O(31)–N(30)–O(33)	121.0(2)	O(42)–N(40)–O(43)	132.0(3)
O(32)–N(30)–O(33)	120.0(2)	O(42)–N(40)–O(43)	103.0(2)

TABLE 5. Bond distances (Å) and bond angles of the sulfonamido moiety in methazolamide and several of its complexes[a]

	S–N	S–O	S–O	O–S–O	O–S–N	O–S–N
Hmacm	1.575	1.420	1.423	120.8	109.6	107.0
1	1.56	1.44	1.42	119.1	110.9	110.9
2	1.520	1.450	1.427	115.9	115.6	111.0
3	1.547	1.432	1.431	116.4	112.8	111.8
4	1.538	1.443	1.443	116.3	114.3	111.1
5	1.540	1.445	1.439	116.4	114.0	111.0

[a] **1** = $[Co(macm)(aib)_2(NH_3)](NO_3)_2 \cdot 2H_2O$; **2** = $Ni(macm)_2(NH_3)_4$ [9]; **3** = $Cu(macm)_2(py)_2(OH_2)_2$; **4** = $Ni(macm)_2(py)_2(OH_2)_2$; **5** = $Co(macm)_2(py)_2(OH_2)_2$ [10].

The nitrate ions and the water molecules are not coordinated and contribute to the packing by forming an intricate hydrogen bond system involving the coordinated ammonia and aib molecules.

Spectroscopic results

The IR spectrum of the complex exhibits bands for ionic nitrate at 1760 and 1390 cm^{-1}. A continuous absorption at 3500–3400 cm^{-1} is attributable to the presence of lattice water. The most relevant bands are those at 1310 and 1140 cm^{-1}, sharp and intense, assigned to the $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ vibrations, respectively. The asymmetric vibration is not modified with respect to the equivalent in the ligand, whereas the symmetric vibration is shifted to lower frequencies. The band at 960 cm^{-1}, due to the ν(S–N) mode, appears at higher frequencies compared to that of the ligand, as a result of the coordination via the N atom of the sulfonamido group. The intense and splitted band between 1610 and 1590 cm^{-1} must include the $\nu(C{=}O)$ and δ(N–H) vibrations of methazolamide, aib and the ammonia ligands. According to the crystal structure, the $\nu(C{=}O)$ band does not change. At 1660 cm^{-1} a new band is observed. In agreement with the literature [23, 24] this absorption could be attributed to the $\nu(C{=}N)$ mode of aib molecules. In the far-IR region the new bands at 460, 410 and 340 cm^{-1} are assigned to $\nu(Co\text{–}NH_3)$, $\nu(Co\text{–}NH_2)$ and ν(Co–NH) vibrations, respectively.

The electronic spectra are in accord with an octahedral geometry around the Co(III) centre. The solid reflectance spectrum of the complex presents two low spin d–d bands at 21 100 and at 28 700 cm^{-1}, which are assigned to $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ electronic transitions.

Supplementary material

Tables of positional parameters and their estimated standard deviations, general displacement parameters, and least-squares planes and structure factors, are available from the authors on request.

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