

## Short Communication

### Synthesis and characterization of mononuclear complexes containing 3-acetylamino-1,2,4-triazole (aat). X-ray structure of $[\text{Co}(\text{aat})_2(\text{H}_2\text{O})_2]\text{Br}_2$

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#### Abstract

The spectroscopic characteristics of the isostructural compounds  $[\text{M}(\text{aat})_2(\text{H}_2\text{O})_2]\text{X}_2$  (aat=3-acetylamino-1,2,4-triazole; M=Co, Cu, X=Br, Cl; M=Ni, X=Cl) are described. The structure of  $[\text{Co}(\text{aat})_2(\text{H}_2\text{O})_2]\text{Br}_2$  has been determined by X-ray diffraction methods. Crystals are monoclinic, space group  $P2_1/a$  with  $a=9.686(3)$ ,  $b=14.433(4)$ ,  $c=6.169(2)$  Å,  $\beta=92.84(2)^\circ$  and  $Z=2$ . The structure was refined to final  $R$  and  $R'$  values of 0.033 and 0.039 for 1066 observed reflections. In the mononuclear cationic complex, having an imposed crystallographic  $C_2$  symmetry, the cobalt atom is surrounded in a slightly distorted octahedral arrangement by two axial water molecules (Co–Ow=2.108(5) Å) and in the equatorial plane by two oxygen atoms (Co–O(1)=2.100(4) Å) and two triazole nitrogen atoms (Co–N(3)=2.063(5) Å) from two aat chelating ligands. The complex cations are associated in chains, with interposed bromide anions, by hydrogen bonding system.

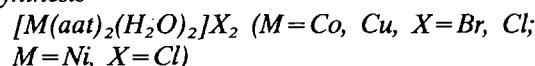
#### Introduction

Triazole systems are of interest in coordination chemistry from different points of view. First, because of their numerous applications: some triazole derivatives have been reported to act as antimicrobial, antiphlogistic

or cytostatic agents [1]; a wide range of triazole compounds exhibit activity against phytopathogenic fungi [2, 3]; 5-amino-1,2,4-triazole is the precursor of additives used in photography and products with known anti-corrosion properties [4, 5]. In these industrial, medical and biological processes metal ions are involved, but not much is known about their interaction with the triazole ligands. On the other hand, an enormous amount of work has been done on the 1,2,4-triazole derivatives due to their versatility as ligands and their metal centres-bridging properties [6, 7]. Several different types of polynuclear complexes have been described [8–13]. The ligand aat (3-acetylamino-1,2,4-triazole) is being studied because of the many different chelating and bridging possibilities that it offers taking into account that the substituent on position 3 is also a coordinating ligand. Furthermore, aat is capable of acting as a ligand either with or without deprotonation (which, in turn, can take place either on the ring and/or the acetamido group). Although from the structure of the aat polynuclear complexes are expected to be formed, the influence of the conditions of synthesis, the metal ion and the anion, can lead to the isolation of mononuclear species. Up to now, only copper(II) compounds of aat have been reported: the mononuclear  $[\text{Cu}(\text{aat})_2(\text{H}_2\text{O})_2]\text{SO}_4 \cdot 5\text{H}_2\text{O}$  [14] and the linkage isomers (also mononuclear)  $[\text{Cu}(\text{aat})_2(\text{NCS-}N)_2]$  and  $[\text{Cu}(\text{aat})_2(\text{NCS-}S)_2]$  [15]. Their crystal structures have shown aat behaving as a bidentate chelating ligand. We now investigate the coordination mode of aat towards Co(II), Cu(II) and Ni(II) in the presence of  $\text{Br}^-$  or  $\text{Cl}^-$  anions.

#### Experimental

##### Synthesis



The aat ligand was synthesized as indicated by van den Bos [16] and recrystallized from boiling water. Orange crystals of  $[\text{Co}(\text{aat})_2(\text{H}_2\text{O})_2]\text{Br}_2$  (I) were obtained by dissolving 4 mmol of  $\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$  and 4 mmol of aat in 40 ml of water, followed by filtration. The remaining wine-red solution was allowed to stand at room temperature. Prismatic crystals suitable for X-ray analysis were observed after *c.* 1 month. *Anal.* Calc. for  $\text{C}_8\text{H}_{16}\text{Br}_2\text{CoN}_8\text{O}_4$  (MW=507.0): C, 19.0; H, 3.2; N, 22.1; Br, 31.5; Co, 11.6. Found: C, 18.8; H, 3.2; N, 22.4; Br, 30.4; Co, 11.1%.

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Crystals of  $[\text{Co}(\text{aat})_2(\text{H}_2\text{O})_2]\text{Cl}_2$  (**II**),  $[\text{Cu}(\text{aat})_2(\text{H}_2\text{O})_2]\text{Cl}_2$  (**III**),  $[\text{Cu}(\text{aat})_2(\text{H}_2\text{O})_2]\text{Br}_2$  (**IV**) and  $[\text{Ni}(\text{aat})_2(\text{H}_2\text{O})_2]\text{Cl}_2$  (**V**) were obtained by dissolving 4 (**II**) or 2 (**III**, **IV**, **V**) mmol of the corresponding M(II) salt and 4 mmol of aat in 40 (**II**) or 25 (**III**, **IV**, **V**) ml of water, followed by filtration. *Anal. Calc.* for  $\text{C}_8\text{H}_{16}\text{Cl}_2\text{CoN}_8\text{O}_4$  (**II**) (MW = 462.5): C, 25.2; H, 3.2; N, 29.3; Cl, 18.6; Co, 15.4. Found: C, 24.0; H, 4.0; N, 26.8; Cl, 17.2; Co, 16.4%. Calc. for  $\text{C}_8\text{H}_{16}\text{Cl}_2\text{CuN}_8\text{O}_4$  (**III**) (MW = 467.2): C, 22.7; H, 3.8; N, 26.5; Cl, 16.8; Cu, 15.0. Found: C, 23.2; H, 3.9; N, 27.2; Cl, 16.5; Cu, 14.7%. Calc. for  $\text{C}_8\text{H}_{16}\text{Br}_2\text{CuN}_8\text{O}_4$  (**IV**) (MW = 511.8): C, 18.8; H, 3.2; N, 21.9; Br, 31.2; Cu, 12.4. Found: C, 18.6; H, 3.2; N, 22.2; Br, 31.7; Cu, 12.4%. Calc. for  $\text{C}_8\text{H}_{16}\text{Cl}_2\text{NiN}_8\text{O}_4$  (**V**) (MW = 462.3): C, 23.0; H, 3.9; N, 26.8; Cl, 17.0; Ni, 14.1. Found: C, 23.0; H, 3.9; N, 26.9; Cl, 16.7; Ni, 14.8%.

#### Spectroscopic measurements

IR spectra were obtained with a Perkin-Elmer model 580B IR spectrophotometer in the region 4000–180  $\text{cm}^{-1}$  as KBr pellets. Ligand field spectra were recorded in the region 28 000–4000  $\text{cm}^{-1}$  on a Perkin-Elmer 330 UV-Vis spectrophotometer, by the diffuse-reflectance technique with MgO as reference.

#### X-ray structure determination of complex I

Experimental data for the X-ray analysis are shown in Table 1. The X-ray data collection was carried out at room temperature. Cell dimensions were obtained from 30 reflections with  $\theta$  angle in the range 10.13–19.03°. Correction for absorption effects was applied using the program ABSORB [17] at the end of the isotropic refinements. The absorption coefficients  $T$  as a function of the two polar angles  $\phi$  and  $\mu$  of the incident and diffracted beam paths are in the range  $1.192 \leq T \leq 0.671$ .

The structure was solved by Patterson and Fourier methods and refined using the SHELX package of crystallographic computer programs [18]. H atom positions, found from  $\Delta F$  synthesis, were refined with isotropic temperature factors. Full matrix least-squares refinement on 138 parameters converged to yield agreement indices  $R = 0.0333$ ,  $R_w = 0.0390$  ( $w = 0.3123 [ \sigma^2(F_o) + 0.001624F_o^2 ]^{-1}$ ). Table 2 lists the atomic coordinates of compound I. Geometrical calculations were performed using PARST [19]. The atomic scattering factors were taken from the literature [20].

## Results and discussion

#### Crystal structure

The structure of  $[\text{Co}(\text{aat})_2(\text{H}_2\text{O})_2]\text{Br}_2$  (**I**) is reported. The following compounds were also synthesized and analysed:  $[\text{Co}(\text{aat})_2(\text{H}_2\text{O})_2]\text{Cl}_2$  (**II**),  $[\text{Cu}(\text{aat})_2(\text{H}_2\text{O})_2]\text{Cl}_2$

TABLE 1. Experimental data for the crystallographic analyses

Formula	$\text{C}_8\text{H}_{16}\text{Br}_2\text{CoN}_8\text{O}_4$
Molecular weight	507.007
Crystal system	monoclinic
Space group	$P2_1/a$
Radiation	graphite monochromatized Mo K $\alpha$
$\lambda$ (Å)	0.71073
$a$ (Å)	9.686(3)
$b$ (Å)	14.433(4)
$c$ (Å)	6.169(2)
$\beta$ (°)	92.84(2)
$V$ (Å <sup>3</sup> )	861.4(5)
$Z$	2
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.955
$F(000)$	498
Crystal size (mm)	0.13 × 0.10 × 0.22
Linear absorption (cm <sup>-1</sup> )	56.19
Diffractometer	Philips PW 1100
Scan type	$\omega/2\theta$
Scan speed (°/min)	3–12
Scan width	$(\theta - 0.60) - (\theta + 0.60 + 0.346 \tan \theta)$
2 $\theta$ Range (°)	6–54
Reflections measured	$\pm h, k, l$
Standard reflection	one measured after 50 reflections
Unique total data	2131
Unique observed data ( $I \geq 2\sigma(I)$ )	1066
No. variables	138
$R$	0.0333
$R_w$	0.0390

TABLE 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{Å}^2 \times 10^4$ ) (one third trace of the diagonalized matrix), with e.s.d.s in parentheses

Atom	$x/a$	$y/b$	$z/c$	$U_{\text{eq}}$
Co	5000	0	0	243(4)
Br	1302.3(7)	1912.2(5)	1205.2(13)	378(2)
Ow	5525(5)	-1215(3)	-1670(8)	372(16)
O(1)	3765(4)	-781(3)	2025(7)	336(15)
N(1)	1671(6)	497(4)	-4422(9)	342(19)
N(2)	975(5)	-48(4)	-3041(9)	337(18)
N(3)	3222(5)	106(4)	-1969(8)	267(17)
N(4)	1704(6)	-849(4)	130(9)	315(18)
C(1)	1965(6)	-260(4)	-1597(10)	259(19)
C(2)	2974(7)	575(5)	-3785(11)	306(22)
C(3)	2581(6)	-1090(4)	1777(10)	273(20)
C(4)	2031(8)	-1771(5)	3327(12)	386(26)
H(1)	1202(74)	707(45)	-5567(120)	755(212)
H(2)	3612(78)	944(47)	-4570(123)	74(228)
H(4)	782(72)	-1079(52)	-126(114)	542(219)
H(41)	941(74)	-1658(48)	3209(117)	995(213)
H(42)	1904(71)	-2495(54)	2820(113)	963(210)
H(43)	2680(78)	-1648(46)	4701(129)	1177(215)
H(1Ow)	6391(76)	-1419(51)	-1276(115)	679(227)
H(2Ow)	5168(80)	-1717(51)	-1499(126)	880(219)

(III),  $[\text{Cu}(\text{aat})_2(\text{H}_2\text{O})_2]\text{Br}_2$  (IV) and  $[\text{Ni}(\text{aat})_2(\text{H}_2\text{O})_2]\text{Cl}_2$  (V). Crystals of I, III and IV are isostructural from unit cell parameter X-ray determinations (crystals of II and V were not suitable for this type of analysis). On the other hand, all compounds (I–V) are isostructural on the basis of their IR spectra.

Compound I can be described by centrosymmetrical cations  $[\text{Co}(\text{aat})_2(\text{H}_2\text{O})_2]^{2+}$  and  $\text{Br}^-$  counteranions joined together by hydrogen bonding. A view of the cationic complex with the related atomic numbering scheme is shown in Fig. 1. Relevant bond distances and angles are given in Table 3. The slightly distorted octahedral coordination of Co involves, mutually *trans*, two water molecules and in equatorial positions two O(1) and two N(3) atoms from two aat chelating ligands. The six-membered chelate rings, in which the bite angle

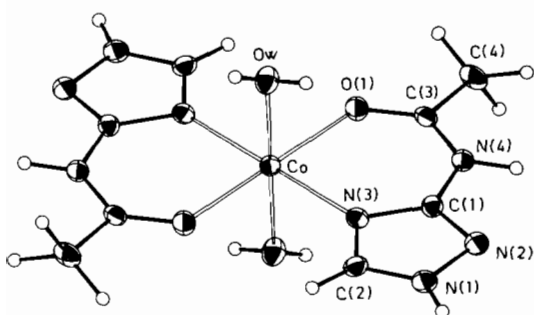


Fig. 1. Perspective view of the  $[\text{Co}(\text{aat})_2(\text{H}_2\text{O})_2]^{2+}$  cationic complex with the atomic numbering scheme. Thermal ellipsoids at 30% probability level.

TABLE 3. Bond distances (Å) and angles (°) with e.s.d.s in parentheses and hydrogen bonds for compound I

Co–Ow	2.108(5)	N(2)–C(1)	1.312(8)	
Co–O(1)	2.100(4)	N(3)–C(1)	1.358(8)	
Co–N(3)	2.063(5)	N(3)–C(2)	1.321(8)	
O(1)–C(3)	1.233(7)	N(4)–C(1)	1.396(8)	
N(1)–N(2)	1.362(8)	N(4)–C(3)	1.338(8)	
N(1)–C(2)	1.308(9)	C(3)–C(4)	1.488(10)	
O(1)–Co–N(3)	84.6(2)	C(1)–N(4)–C(3)	127.3(6)	
Ow–Co–N(3)	89.4(2)	N(3)–C(1)–N(4)	124.3(5)	
Ow–Co–O(1)	90.2(2)	N(2)–C(1)–N(4)	120.4(6)	
Co–O(1)–C(3)	132.4(4)	N(2)–C(1)–N(3)	115.2(6)	
N(2)–N(1)–C(2)	111.3(5)	N(1)–C(2)–N(3)	110.1(6)	
N(1)–N(2)–C(1)	101.0(5)	O(1)–C(3)–N(4)	123.5(6)	
Co–N(3)–C(2)	130.5(4)	N(4)–C(3)–C(4)	115.2(6)	
Co–N(3)–C(1)	126.9(4)	O(1)–C(3)–C(4)	121.3(6)	
C(1)–N(3)–C(2)	102.4(5)			
D–H···A	D–H	D···A	H···A	D–H···A
N(1)–H(1)···Br <sup>i</sup>	0.87(7)	3.389(6)	2.65(7)	143(6)
N(1)–H(1)···N(2) <sup>ii</sup>	0.87(7)	3.007(7)	2.43(7)	124(6)
N(4)–H(4)···Br <sup>iii</sup>	0.96(7)	3.358(6)	2.42(7)	168(6)
Ow–H(1Ow)···Br <sup>iv</sup>	0.91(7)	3.233(5)	2.34(7)	166(6)
Ow–H(2Ow)···Br <sup>v</sup>	0.81(7)	3.252(5)	2.45(7)	169(7)

Symmetry operations: <sup>i</sup> $x, y, -1+z$ ; <sup>ii</sup> $-x, -y, -1-z$ ; <sup>iii</sup> $-x, -y, -z$ ; <sup>iv</sup> $1-x, -y, -z$ ; <sup>v</sup> $\frac{1}{2}-x, -\frac{1}{2}+y, -z$ .

is  $84.7(2)^\circ$ , and the other non-H atoms (excluding the methyl carbon atom) of aat are nearly coplanar. The geometrical parameters of aat indicate an extensive conjugation in the ligand.

The Co–Ow axial distance (2.108(5) Å) and the equatorial Co–O(1) and Co–N(3) bond lengths (2.100(4) and 2.063(5) Å, respectively) agree well with the values in the literature for similar slightly distorted octahedral coordination of Co(II) atom.

The complexes are associated in chains (see Table 3 and Fig. 2) by pairs of hydrogen bonds involving the H-bond donor N(1) and H-bond acceptor N(2) atoms from centrosymmetrically related units. The uncoordinated  $\text{Br}^-$  anions interpose between these chains connecting them by hydrogen bonding which involve the N(1) and N(4) atoms from the aat ligands and the coordinated water molecules.

The position of the triazole active hydrogen suggests that the aat molecule, which behaves as a neutral ligand, can be considered a tautomer form with respect to the parent 5-amino-1,2,4-triazole system [21]. A similar situation has been found for the undeprotonated aat ligand in the previously investigated compound  $[\text{Cu}(\text{aat})_2(\text{H}_2\text{O})_2]\text{SO}_4 \cdot 5\text{H}_2\text{O}$  (VI) [14] and linkage isomers  $[\text{Cu}(\text{aat})_2(\text{NCS})_2]$  [15], which contain, with respect to the present complex, a different counterion and additional crystallization water molecules (VI).

In the structure of VI, which crystallizes in the monoclinic system, space group  $P2_1/a$  the same as compound I, the configuration of the cationic complex and the geometrical parameters of aat are similar to the corresponding ones found in I. However, the present complex shows less distortion in the metal octahedral

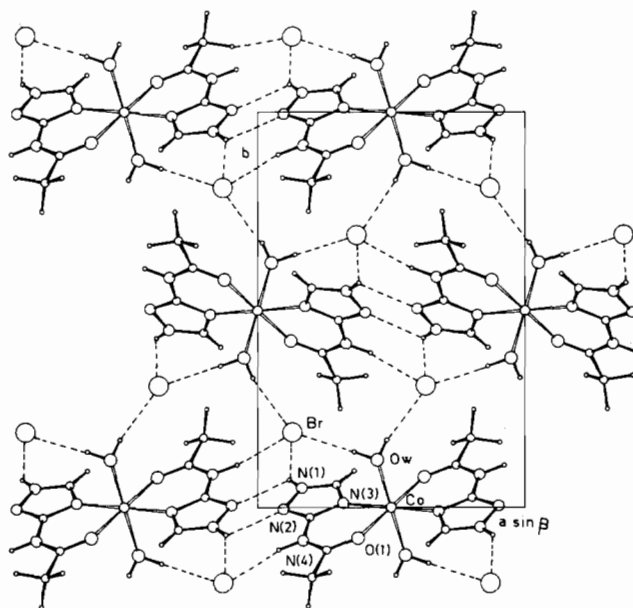


Fig. 2. Projection along  $c$  of  $[\text{Co}(\text{aat})_2(\text{H}_2\text{O})_2]\text{Br}_2$ .

environment (as expected from the Cu(II) Jahn–Teller effect), the axial and equatorial metal–donor distances being closely comparable. Moreover the axial water ligands act only as H-bond donors in **I** and both as H-bond donors and H-bond acceptors in **VI**. Notice that in **VI** but not in **I–V** lattice water molecules are present. (Obviously,  $\text{SO}_4^{2-}$  packs differently from a halide ion.)

The stabilization, in the structure of the Co–aat and Cu–aat derivatives, of one of the two possible tautomeric forms of aat, different from that found for the parent 5-amino-1,2,4-triazole, can be due, as already pointed out for **VI**, to electronic effects induced by the  $\text{N}^4$  coordination or/and to the influence of hydrogen bonding. In the Co–aat derivative pairs of centrosymmetrical hydrogen bridges,  $\text{N}^1\text{--H}\cdots\text{N}^2$ , between aat molecules from neighbouring complexes are present; these bridges involve bifurcated  $\text{N}^1\text{--H}$  groups which allow  $\text{Br}^-$  anions to interact strongly with cationic complexes of the same chain.

Packing forces seem important in promoting the H-bond acceptor behaviour of the potential bridging  $\text{N}^2$  atom of the neutral aat ligand, in both the Cu(II) and Co(II) compared complexes.

#### Spectroscopic characterization

The compounds reported have been characterized by means of IR and UV–Vis spectroscopy.

Table 4 lists the most significant changes observed in the IR spectra with respect to the parent aat. The shifts to lower frequencies are in agreement with coordination through the carbonyl O atom and one of the ring N atoms. It should be noted that the KBr/IR spectrum of microcrystalline powder of **I** does not show bands around  $3400\text{--}3500\text{ cm}^{-1}$ , although there is water in the coordination sphere. (The assignments have been given following refs. 22–24.)

Table 5 displays the electronic spectra bands and the corresponding assignments [25]. The values of the maxima are in accordance with an octahedral environment around the metal ion in every case. The isomorphism of compounds **II** and **V**, not checked by the powder X-ray diffraction technique, has been shown

TABLE 4. Selected IR bands ( $\text{cm}^{-1}$ )

Compound	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N}) + \delta(\text{N}=\text{H})$
aat	1685s	1622s, 1556s
<b>I</b>	1660–1635(sp)s	1605s, 1545vw
<b>II</b>	1660–1640(sp)s	1605s, 1545vw
<b>III</b>	1651–1636(sp)s	1609s, 1536vw
<b>IV</b>	1650–1635(sp)s	1605s, 1540vw
<b>V</b>	1658s	1608s, 1544vw
<b>VI</b> (ref. 14)	1649–1634(sp)s	1606s, 1535vw

s=strong, v=very, w=weak, sp=split or doublet.

TABLE 5. Electronic spectra maxima ( $\text{cm}^{-1}$ )

Compound	$\lambda_{\text{max}}$
<b>I</b>	25.600(sh), 20.535s ( $\nu_3$ ), 11.085 ( $\nu_1$ )
<b>II</b>	25.510(sh), 20.535s ( $\nu_3$ ), 11.310 ( $\nu_1$ )
<b>III</b>	14.390s, 11.310(sh)
<b>IV</b>	14.410s, 11.310(sh)
<b>V</b>	28.250s ( $\nu_3$ ), 16.155s ( $\nu_2$ ), 10.400b ( $\nu_1$ )
<b>VI</b> (ref. 14)	14.815s, 11.820(sh)

b=broad band with maximum not well defined, s=strong, sh=shoulder.

by the strict similarity of their IR spectra. We have therefore concluded that compounds **II** and **V** are IR isostructural with respect to compound **I**, whose structure is described here.

#### Supplementary material

Additional material comprising all bond distances and angles, thermal parameters and structure factor amplitudes are available from authors on request.

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