

Benzotriazole Complexes. III. The Crystal Structure of a Trinuclear Benzotriazolate Ammine Complex of Nickel(II)

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The crystal structure of the title compound, $[\text{Ni}_3(\text{C}_6\text{H}_4\text{N}_3)_6(\text{NH}_3)_6] \cdot 2(\text{CH}_3)_2\text{CO} \cdot 2\text{H}_2\text{O}$, has been investigated by X-ray diffraction techniques. The crystals are monoclinic, space group $P2_1/n$, with $a=10.747(3)$ Å, $b=19.394(3)$ Å, $c=13.925(3)$ Å and $\beta=110.74(4)^\circ$. The structure was refined to $R=0.041$. The complex which has 1 crystallographic symmetry, is trinuclear, the central nickel atom being joined to each terminal nickel atom by three planar benzotriazolate group bridges. Three molecules of ammonia complete the octahedral coordination of the terminal nickel atoms. The average distances are: Ni(central)–N1, 2.107(2) Å, Ni(terminal)–N2, 2.082(3) Å and Ni–N(ammonia), 2.139(5) Å. The Ni–Ni separation is 3.711(1) Å.

The present structure analysis is part of an investigation of benzotriazole complexes.^{1,2} Benzotriazolyl is henceforth referred to as BTA.

EXPERIMENTAL

Pale purple crystals of $\text{Ni}_3(\text{BTA})_6(\text{NH}_3)_6 \cdot 2(\text{CH}_3)_2\text{CO} \cdot 2\text{H}_2\text{O}$ were precipitated by mixing 2×10^{-4} mol nickel chloride hexahydrate in 2 ml 7 M ammonia with 3×10^{-3} mol benzotriazole in 6–8 ml acetone. Besides the title compound another compound was precipitated. It was trigonal, with $a=32.800(9)$ Å and $c=17.386(5)$ Å, space group $R\bar{3}$ or $R\bar{3}$, but has not been further investigated. The crystals are unstable in air at room temperature, and the crystals used for X-ray work were therefore covered by glue. Determination of the possible space groups and the data collection were carried out as described in Ref. 1. The dimensions of the crystal were $0.33 \times 0.23 \times 0.20$ mm. The structure was solved by Patterson technique.³ The refinement

technique and the references to the atomic scattering factors are those used in Ref. 1. Only the hydrogen atoms of the BTA ligands were included in the refinement of the structure. Crystal data and R -values are listed in Table 1. The final positional parameters with estimated standard deviations are listed in Table 2. The labelling of the atoms are shown in Fig. 1. Lists of thermal parameters as well as lists of observed and calculated structure factors may be obtained from the authors on request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Bond lengths and bond angles with their estimated standard deviations are listed in Tables 3 and 4.

Table 1. Crystal data.

M	1139.4
$\mu(\text{MoK}\alpha)(\text{cm}^{-1})$	10.9
Crystal system	monoclinic
$V(\text{Å}^3)$	2714.3
$a(\text{Å})$	10.747(3)
$b(\text{Å})$	19.394(3)
$c(\text{Å})$	13.925(3)
$\beta(^\circ)$	110.74(4)
Space group	$P2_1/n$
$D_c(\text{g cm}^{-3})$	1.39
Z	2
Total number of reflections	4756
Number of independent observations	3255
$[I \geq \sigma(I)]$	
$R = \frac{\sum F_o - F_c }{\sum F_o }$	0.041
$R_w = \left[\frac{\sum w(F_o - F_c)^2}{\sum w F_o ^2} \right]^{1/2}$	0.055

Table 2. Final atomic coordinates $\times 10^4$. The estimated standard deviations $\times 10^4$ are in parentheses. The values of the hydrogen atoms are multiplied by 10^3 .

Atom	x	y	z	Atom	x	y	z		
Ni1	0	0	0	Ni2	2264(1)	1495(1)	308(1)		
C1	5970(7)	3343(3)	700(5)	N4	4386(4)	1409(2)	820(3)		
C2	7321(10)	3105(7)	1326(8)	N5	2393(4)	2376(2)	1252(3)		
C3	5876(9)	4051(5)	267(7)	N6	2405(4)	2153(2)	-892(3)		
O1	4973(5)	2999(3)	519(5)	O2	5273(5)	1784(4)	3499(7)		
BTA1			BTA2			BTA3			
N1	1448(3)	300(2)	1404(2)	-646(3)	1029(2)	-333(3)	1357(3)	108(2)	-773(2)
N2	2243(3)	844(2)	1493(2)	195(3)	1564(2)	-210(3)	2122(3)	663(2)	-665(3)
N3	3081(4)	935(2)	2450(3)	-454(4)	2156(2)	-484(3)	2856(3)	647(2)	-1259(3)
C4	2820(4)	421(2)	3013(3)	-1768(4)	1999(2)	-806(3)	2557(4)	38(2)	-1773(3)
C5	1787(4)	21(2)	2360(3)	-1900(4)	1297(2)	-712(3)	1611(4)	-303(2)	-1478(3)
C6	1316(5)	-558(2)	2740(4)	-3168(4)	984(3)	-992(4)	1115(5)	-950(2)	-1889(4)
C7	1915(6)	-707(3)	3762(4)	-4235(5)	1410(3)	-1382(5)	1602(6)	-1220(3)	-2596(4)
C8	2934(6)	-299(3)	4415(4)	-4107(5)	2127(3)	-1503(5)	2557(6)	-877(3)	-2895(4)
C9	3417(6)	267(3)	4077(4)	-2904(5)	2430(3)	-1221(5)	3038(5)	-253(3)	-2503(4)
H2	78(5)	-86(3)	234(4)	-322(5)	53(3)	-92(4)	47(6)	-116(3)	-172(4)
H3	160(5)	-115(3)	401(4)	-506(6)	123(3)	-163(5)	128(6)	-168(3)	-283(4)
H4	338(6)	-43(3)	506(5)	-493(6)	243(3)	-199(4)	297(7)	-108(4)	-330(5)
H5	420(6)	63(3)	451(4)	-276(5)	293(3)	-129(4)	373(7)	-11(3)	-264(5)

Table 3. Bond distances (Å) and bond angles (°) with estimated standard deviations in the nickel coordination spheres. The figures in parentheses refer to the number of the BTA ligands.

Atoms	Distance or angle
Ni1 - N1(1)	2.104(3)
Ni1 - N1(2)	2.110(3)
Ni1 - N1(3)	2.108(4)
N1(1) - Ni1 - N1(2)	91.2(1)
N1(1) - Ni1 - N1(3)	91.7(1)
N1(2) - Ni1 - N1(3)	91.6(1)
Ni2 - N4	2.141(4)
Ni2 - N5	2.131(4)
Ni2 - N6	2.150(5)
Ni2 - N2(1)	2.085(4)
Ni2 - N2(2)	2.085(3)
Ni2 - N2(3)	2.077(3)
N4 - Ni2 - N5	91.6(2)
N4 - Ni2 - N6	86.9(2)
N4 - Ni2 - N2(1)	89.9(2)
N4 - Ni2 - N2(3)	88.7(1)
N5 - Ni2 - N6	89.8(2)
N5 - Ni2 - N2(1)	90.8(2)
N5 - Ni2 - N2(2)	89.5(2)
N6 - Ni2 - N2(2)	93.1(1)

Table 3. Continued.

N6 - Ni2 - N2(3)	87.9(1)
N2(1) - Ni2 - N2(2)	90.2(1)
N2(1) - Ni2 - N2(3)	91.6(1)
N2(2) - Ni2 - N2(3)	90.1(1)

The structure consists of trinuclear $\text{Ni}_3(\text{BTA})_6$ - $(\text{NH}_3)_6$ units as indicated in Fig. 2. These units have $\bar{1}$ crystallographic symmetry, with Ni1 located on a center of symmetry. This central Ni atom is joined to each of the other two by three bridging BTA groups. The BTA ligands are coordinated to Ni1 via N1 and to Ni2 via N2. Thus the central Ni

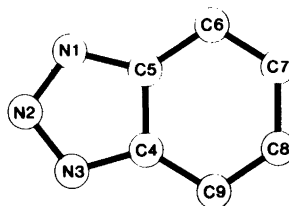


Fig. 1. The benzotriazole anion.

Table 4. Bond distances (Å) and bond angles (°) with estimated standard deviations in the BTA ligands.

Atoms	BTA 1 Distance or angle	BTA 2 Distance or angle	BTA 3 Distance or angle
N1–N2	1.335(5)	1.346(4)	1.331(4)
N2–N3	1.330(4)	1.329(5)	1.329(6)
N3–C4	1.358(6)	1.356(6)	1.359(5)
C4–C5	1.395(5)	1.380(6)	1.391(7)
C5–N1	1.362(5)	1.365(5)	1.363(6)
C5–C6	1.409(7)	1.414(6)	1.404(6)
C6–C7	1.370(7)	1.361(7)	1.372(9)
C7–C8	1.395(8)	1.412(8)	1.404(10)
C8–C9	1.367(9)	1.346(8)	1.351(8)
C9–C4	1.422(7)	1.422(7)	1.412(8)
C6–H2	0.88(5)	0.90(5)	0.90(7)
C7–H3	1.03(6)	0.90(6)	0.96(6)
C8–H4	0.89(6)	1.08(5)	0.93(8)
C9–H5	1.09(5)	0.99(6)	0.88(8)
C5–N1–N2	106.4(3)	106.4(3)	106.3(4)
N1–N2–N3	112.5(3)	111.7(3)	112.9(3)
N2–N3–C4	106.0(3)	106.2(3)	105.5(4)
N3–C4–C5	108.1(3)	108.7(3)	108.5(4)
C4–C5–N1	107.0(4)	107.0(3)	106.8(3)
C4–C5–C6	120.4(4)	121.2(4)	121.0(5)
C5–C6–C7	117.3(4)	116.3(4)	116.6(5)
C6–C7–C8	122.0(5)	122.7(5)	122.5(5)
C7–C8–C9	122.5(5)	121.3(5)	121.3(6)
C8–C9–C4	116.1(5)	117.4(5)	117.6(6)
C9–C4–C5	121.6(5)	121.0(4)	121.1(4)

atom has an octahedral coordination with six Ni–N1 bonds [average distance 2.107(2) Å], while the two terminal Ni atoms have an octahedral coordination with three Ni–N2 bonds [2.082(3) Å] and three Ni–N(ammonia) bonds [2.139(5) Å]. The Ni2–N2 bonds are somewhat shorter than the Ni1–N1 bonds. The same feature is found in hexakis(benzotriazolato)hexakis(allylamine)trickel(II),⁴ the two bond lengths being 2.062(5) Å and 2.127(5), respectively. The Ni–Ni separation in

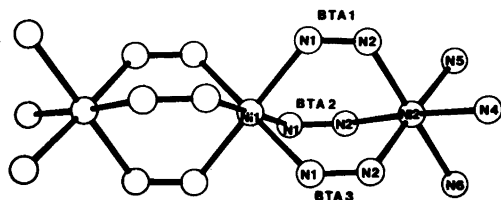


Fig. 2. The coordination around the Ni atoms. Ni1 is located on a center of symmetry.

the latter structure is 3.73 Å, which is in good agreement with the value of 3.711 Å found in the present structure.

The packing of the structure is shown in Fig. 3. Water and acetone molecules of solvation are located between the trinuclear units. The non-hydrogen atoms of the acetone molecule are coplanar (deviations less than 0.01 Å), with an O1–C1 bond of 1.211(9) Å, a C1–C2 bond of 1.478(11) Å and a C1–C3 bond of 1.490(11) Å. The angles in the acetone molecule are 124.3(8), 116.0(8) and 119.7(6)° for the O1–C1–C2, C2–C1–C3 and C3–C1–O1 angles, respectively. The BTA2 ligand lies perpendicular to the *bc*-plane, while the angles between the *bc*-plane and the planes through BTA1 and BTA3 are 47.8 and 42.9°, respectively.

The hydrogen-bonding distances involving the water molecule (O2) are the O2–N3[BTA1($\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$)] distance [2.760(10) Å], the O2–N3 (BTA1) distance [2.821(7) Å], and the O2–N6($\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$) distance [2.974(7) Å]. The hydrogen-

Table 5. Comparison of the BTA ligand in $[\text{Ni}_3(\text{BTA})_6(\text{NH}_3)_6] \cdot 2(\text{CH}_3)_2\text{CO} \cdot 2\text{H}_2\text{O}$ with benzotriazole and BTA ligands in some other compounds. Average values of three independent molecules for $[\text{Ni}_3(\text{BTA})_6(\text{NH}_3)_6] \cdot 2(\text{CH}_3)_2\text{CO} \cdot 2\text{H}_2\text{O}$ and four independent molecules for benzotriazole.

Distance (Å) or angle(°)	$[\text{Ni}_3(\text{BTA})_6(\text{NH}_3)_6]$ bidentate(N1,N2)	$[\text{Zn}_2(\text{BTA})_4]$ _n bidentate(N1,N3) ²	$[\text{Ni}_3(\text{BTA})_6(\text{AA})_6]$ bidentate(N1,N2) ⁴	$[\text{Ir}(\text{BTA})\text{CO}(\text{PPh}_3)_2]$ monodentate(N1) ⁵	[TIBTA] tridentate ⁶	Benzotriazole ⁷
N1-N2	1.338(5)	1.337(2)	1.333(7)	1.344(6)	1.362(6)	1.346(5)
N2-N3	1.329(1)	1.333(1)	1.328(7)	1.335(6)	1.342(6)	1.310(4)
N3-C4	1.358(1)	1.375(2)	1.339(8)	1.358(7)	1.385(7)	1.377(6)
C4-C5	1.389(5)	1.393(1)	1.396(9)	1.383(7)	1.403(7)	1.389(5)
C5-N1	1.363(1)	1.368(1)	1.385(8)	1.366(6)	1.381(7)	1.366(7)
C5-C6	1.409(3)	1.403(2)	1.431(10)	1.398(7)	1.398(8)	1.404(4)
C6-C7	1.367(3)	1.368(2)	1.386(12)	1.370(8)	1.361(8)	1.367(3)
C7-C8	1.404(5)	1.404(4)	1.417(12)	1.387(9)	1.399(7)	1.405(5)
C8-C9	1.354(6)	1.364(3)	1.399(12)	1.376(9)	1.362(8)	1.368(5)
C9-C4	1.419(3)	1.403(2)	1.437(9)	1.416(8)	1.389(8)	1.409(5)
C5-N1-N2	106.4(1)	108.3(1)	105.5(5)	107.8(4)	106.4(4)	110.3(7)
N1-N2-N3	112.4(4)	109.8(1)	112.7(5)	110.4(4)	111.2(5)	108.8(4)
N2-N3-C4	106.0(2)	108.4(1)	106.7(5)	106.8(4)	107.5(4)	108.2(2)
N3-C4-C5	108.4(2)	106.6(1)	108.5(5)	108.8(5)	106.8(4)	108.4(2)
C4-C5-N1	106.9(1)	107.0(1)	106.5(5)	106.1(4)	108.0(4)	104.2(4)
C4-C5-C6	120.8(3)	121.2(3)	122.5(5)	122.3(5)	119.7(5)	122.7(4)
C5-C6-C7	116.8(3)	116.8(2)	114.5(7)	116.8(6)	118.2(5)	115.3(3)
C6-C7-C8	122.4(2)	121.7(2)	124.6(8)	121.9(7)	121.4(5)	122.7(1)
C7-C8-C9	121.7(4)	122.4(2)	120.3(6)	122.0(6)	121.9(5)	122.2(2)
C8-C9-C4	117.0(5)	116.4(2)	116.6(7)	116.9(6)	117.1(5)	116.2(4)
C9-C4-C5	121.2(2)	121.5(2)	121.1(6)	120.1(5)	121.8(5)	120.9(2)

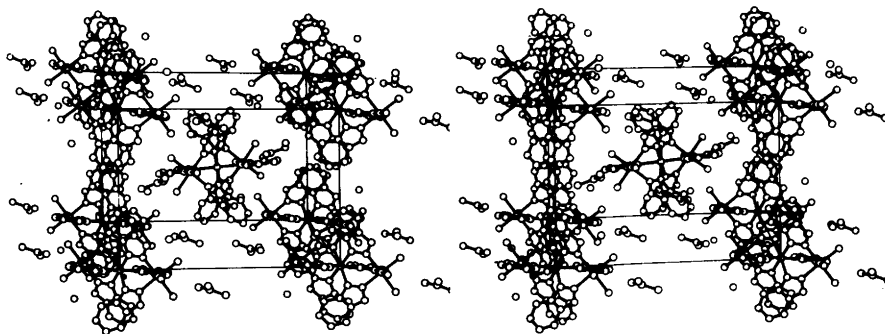


Fig. 3. Stereo view along the *a*-axis of the structure.

bonding distances involving the acetone molecule is found from O1 to N4 [3.205(7) Å], and to N6 [3.213(6) Å].

The BTA ligands are nearly planar, the deviations of the atoms from the least-squares plane through them being less than 0.02 Å. In Table 5 the metrical details of the BTA ligand are compared to those of BTA ligands in other compounds,^{2,4-6} and to those of benzotriazole.⁷ The bond lengths and bond angles in the average groups were found as in Ref. 1. As is the case of $[\text{Zn}_2(\text{BTA})_4]_n$ the BTA ligand nearly has C_{2v} symmetry.

THE EFFECT OF METAL COORDINATION

The geometrical differences in the triazole groups are partly due to differences in charge and partly to differences in coordination. Analysis of the geometry in a series of triazole rings⁸ shows that although the different carbon substituents result in different endocyclic angles at C4 and C5, the sum of the two angles almost exclusively depends on the site of the nitrogen substituents. The same feature but less pronounced is found for the endocyclic angles at the nitrogen atoms. In the case where some of the nitrogen substituents are transition metal ions a gradual change of this site effect should be expected due to differences in the σ -character of the nitrogen-metal bond. In tetrachlorobis-2-[(5-amino-4-carboxamidinium)[1,2,3]triazole]copper(II) monohydrate⁹ the N2–Cu bond does not affect the geometry of the triazole ring, indicating a low σ -character of the bond. In Table 6 idealized values of the sum of the angles at C4 and C5 together with the value of the angle at N2 are listed. The values of the angle at N2 for the 1- and 2-substituted compounds

Table 6. The sum, Σ , of the endocyclic angles at C4 and C5, and the angle at N2 as a function of the sites of nitrogen substitution.

Substitution site	Σ	N2
1	212.7	108.9
2	218.0	117.7
1,2	214.6	~111
1,3	209.5	~103

are corrected for ring closure of the carbon substituents. For the Ni-complexes the result of a comparison is that the angles in the triazole group correspond to a 1,2-substituted compound which indicate a large σ -character of the nitrogen–nickel bonds. The $[\text{Cu}(\text{BTAH})_2\text{Cl}_2]_2$ -compound¹ and the corresponding Zn-compound² may be classified as intermediates between the 1- and 1,3-substituted compounds.

In the other metal complexes with BTA the values of the angles are close to those of 1-substituted triazole. Without knowing the geometry of the free BTA ion, it is, however, difficult to draw any conclusion about the character of the metal–nitrogen bonds. Hopefully, further work in this field will show that this kind of relations may be expressed in a more quantitative way.

Acknowledgement. This work was supported by a grant from the Danish Natural Science Research Council.

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Received March 30, 1981.