ELSEVIER

Inorganica Chimica Acta 227 (1994) 181–184

Inorganica Chimica Acta

Note

Synthesis and X-ray structure of the dinuclear μ-5,5′-diamino-3,3′-bis-1,2,4-triazolato(1 −)-bis(diethylenetriaminecopper(II)) triperchlorate, $[\{Cu(dien)\}_2Hdabt](ClO_4)_3$

Marina Biagini-Cingi [a], Anna Maria Manotti-Lanfredi [a], Franco Ugozzoli [a], Jaap G. Haasnoot [b]

[a] *Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze, 43100 Parma, Italy*

[b] *Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, 2300 RA Leiden, Netherlands*

Received 28 March 1994; revised 1 June 1994

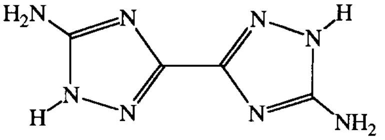
Abstract

The ligand 5,5′-diamino-3,3′-bis-1,2,4-triazole, H_2dabt, forms a mono-anion by abstraction of one H^+. This anion bridges two copper(II) ions. The paper describes the structure of the copper complex $[\{Cu(dien)\}_2Hdabt](ClO_4)_3$ in which the second active hydrogen atom of the ligand is statistically distributed over the two triazole ring N1 atoms. The copper ions of the CuN_5 chromophores are each chelated by a 1,4,7-triazaheptane, (dien), ligand and an N2,N4′ bite of the Hdabt ion. The Cu_2(Hdabt) part of the complex cation, which is located about a crystallographic center of symmetry, is practically planar. The intramolecular copper–copper distance is 5.801(4) Å. The structure has been determined by X-ray diffraction methods. Crystals are monoclinic, space group $P2_1/n$ with $a = 8.389(4)$, $b = 14.931(6)$, $c = 11.967(5)$ Å, $\beta = 97.21(2)°$ and $Z = 2$.

Keywords: Crystal structures; Copper complexes; Triazole ligand complexes; Dinuclear complexes

1. Introduction

1,2,4-Triazole and its derivatives are rather versatile ligands for the syntheses of oligonuclear transition metal compounds. In previous papers we reported on the synthesis and characterization of some complexes containing s-triazole derivatives [1–3]. The bridging nature of the ligand system is brought about by the possibilities of both the N1,N2-bridging mode and the N2,N4 mode. With substituents containing donor atoms, the triazole ring can function as a chelate ligand as well. When two triazole rings are linked together, many coordination sites can be visualized. The symmetrical 3,3′-bis-1,2,4-triazole offers a coordination geometry that is comparable to that of 2,2′-bis-imidazole derivatives. For the bis-imidazoles both mononuclear and dinuclear complexes have been described. As part of our contribution to the study of the coordination mode of the s-triazole derivatives towards transition metals we report here on the dinuclear coordination mode of the 5,5′-diamino derivatives of the 3,3′-bis-1,2,4-triazole ligand system (see Scheme 1).



Scheme 1. The ligand 5,5′-diamino-3,3′-bis-1,2,4-triazole, H_2dabt.

2. Experimental

2.1. Synthesis

Commercially available copper(II) perchlorate hydrate and 1,4,7-triazaheptane (1,5-diamino-3-azapentane) (dien) were used without further purification. 5,5′-Diamino-3,3′-bis-1,2,4-triazole (H_2dabt) was prepared by a literature method [4] from aminoguanidinium hydrogencarbonate and oxalic acid.

SSDI 0020-1693(94)04154-N

The copper complex was prepared by reacting 2 mmol of copper(II) perchlorate in 10 cm^3 of water with 2 mmol of dien. The resulting dark blue solution was filtered and added to a warm solution of 1.5 mmol of H_2dabt in 20 cm^3 ethanol/water 50/50. Dark purple crystals, suitable for X-ray diffraction, formed upon standing at room temperature for three days. The crystals were separated by filtration and washed with a few drops of ethanol/water; they appeared to be stable in air. C, H, N, Cl and Cu analyses, performed by the Microanalytical Laboratory of University College Dublin, appeared to be consistent with the formula $C_{12}H_{31}Cl_3Cu_2N_{14}O_{12}$ for $[\{Cu(dien)\}_2Hdabt](ClO_4)_3$. *Anal.* Found: C, 17.63; H, 3.96; N, 24.33; C, 15.60; Cl, 13.71. Calc.: C, 18.09; H, 3.92; N, 24.61; Cu, 15.95; Cl, 13.35%.

2.2. *X-ray structure determination*

Selected crystallographic data are listed in Table 1. Data were collected at room temperature on a Siemens AED single-crystal diffractometer using nickel-filtered Cu Kα radiation. Cell parameters were obtained from a least-squares fit of 30 reflections in the range $23.54 \leqslant \theta \leqslant 36.74°$. A total of 3087 symmetry-independent reflections ($3 \leqslant \theta \leqslant 70°$) was measured by profile analysis according to the Lehmann and Larsen method [5]; 1313, having $I \geqslant 2\sigma(I)$ (1283 unique reflections; internal $R = 0.02$), were considered observed and used in the analysis. At the end of the isotropic refinement the F_o values were corrected for absorption by the program ABSORB [6]. Maximum and minimum values of the absorption coefficient, as a function of the two polar angles ϕ and μ of the incident and diffracted beam paths, were 1.263 and 0.799, respectively.

Table 1
Experimental data for the crystallographic analysis of $[\{Cu(dien)\}_2Hdabt](ClO_4)_3$

Formula	$C_{12}H_{31}Cl_3Cu_2N_{14}O_{12}$
Molecular weight	796.914
Crystal system	monoclinic
Space group	$P2_1/n$
Radiation	nickel-filtered Cu Kα
λ (Å)	1.54178
a (Å)	8.389(4)
b (Å)	14.931(6)
c (Å)	11.967(5)
β (°)	97.21(2)
Cell volume (Å^3)	1487(1)
Z	2
D_{calc} (g cm^{-3})	1.780
$F(000)$	812
Linear absorption coefficient (cm^{-1})	49.81
Scan type	$\omega/2\theta$
Scan speed (°/min)	3–12
Scan width	$(\theta - 0.60)$–$(\theta + 0.60 + 0.346 \tan \theta)$
Reflections measured	$\pm h, k, l$
No. variables	232
Final R (unit weights)	0.0860

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares methods using the SHELX package of programs [7]. Parameters refined were the overall scale factor, atomic coordinates and anisotropic thermal parameters for all the non-hydrogen atoms with the exception of those of one ClO_4^- anion which is statistically distributed between two different positions (with site occupancy factor (SOF) 0.50), related by a center of symmetry. Eight H atoms were localized in the final ΔF map and refined with isotropic temperature factors. The remaining H atoms, including the hydrogen atom statistically distributed (with SOF 0.50) at N(1), were placed in calculated positions and refined 'riding' on the corresponding carbon or nitrogen atom with isotropic temperature factors. The refinement was stopped at $R = 0.086$ (unit weight). The slightly high R value was due to the poor quality of the single crystals used in the data collection which appeared to be unstable when exposed to the X-ray beam.

The intensity of one standard reflection, collected every hundred, showed a linear decrease of 27% from the beginning to the end of the data collection. A linear scaling factor was then applied to all the reflections to remove the effects of the crystal decay.

Atomic scattering factors, corrected for anomalous dispersion, were taken from Ref. [8]. Final atomic coordinates for the non-hydrogen atoms are given in Table 2. Geometrical calculations were performed using the PARST program [9]. All calculations were carried out on the CRAY X-MP/48 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna.

3. Results and discussion

The structure of $[\{Cu(dien)\}_2Hdabt](ClO_4)_3$ consists of tripositive cations packed together with perchlorate anions. Fig. 1 shows a perspective view of the $[\{Cu(dien)\}_2Hdabt]^{3+}$ complex cation which lies on a crystallographic center of symmetry which coincides with the midpoint of the C(3)–C(3′) bond.

Selected bond distances and angles are given in Table 3. Each Cu atom is coordinated to five nitrogen atoms in a distorted square pyramidal arrangement: the basal plane is formed by the three nitrogen atoms of dien and the N(4) nitrogen atom from the central ligand, the vertex is occupied by nitrogen atom N(2) at a distance of 2.595(13) Å, which can be considered as a semibond interaction. Two symmetry related perchlorate anions have their O(2) and O(2′) atoms close to the unoccupied sixth octahedral coordination sites

Table 2
Fractional atomic coordinates (×10^4) and equivalent thermal parameters (Å^2×10^4) with e.s.d.s in parentheses for the non-hydrogen atoms of [{Cu(dien)}$_2$Hdabt](ClO$_4$)$_3$

	x/a	y/b	z/c	U_{eq}[a]
Cu	116(3)	1374(2)	3299(2)	1073(10)
Cl(1)	2933(5)	3285(3)	2291(4)	991(16)
O(1)	4291(16)	3745(8)	2737(16)	1765(83)
O(2)	2357(23)	2731(10)	3059(12)	1664(80)
O(3)	1785(18)	3936(12)	1902(18)	1988(97)
O(4)	3201(36)	2736(15)	1424(19)	2432(152)
N(1)	3266(14)	199(8)	5897(11)	940(48)
N(2)	1806(16)	−241(7)	5912(11)	899(49)
N(4)	1514(14)	778(7)	4538(9)	782(43)
N(6)	4183(16)	1317(9)	4720(14)	1040(60)
N(11)	−723(14)	2378(8)	4175(10)	927(49)
N(14)	−1558(26)	1761(12)	2084(14)	1302(80)
N(17)	1174(21)	784(9)	2101(11)	1176(66)
C(3)	837(17)	122(9)	5133(14)	878(54)
C(5)	3023(18)	781(9)	5032(13)	798(57)
C(12)	−2251(21)	2700(13)	3514(17)	1139(84)
C(13)	−2138(26)	2622(15)	2316(17)	1294(99)
C(15)	−1009(35)	1627(15)	987(18)	1412(116)
C(16)	−34(39)	826(16)	1051(18)	1512(122)
Cl(2)	4982(12)	211(6)	760(8)	1279(30)
O(5)	5146(23)	598(12)	1884(10)	1147(66)
O(6)	5972(35)	703(18)	61(16)	1985(131)
O(7)	3309(15)	264(25)	268(19)	2683(209)
O(8)	5482(48)	−720(10)	832(20)	2934(415)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

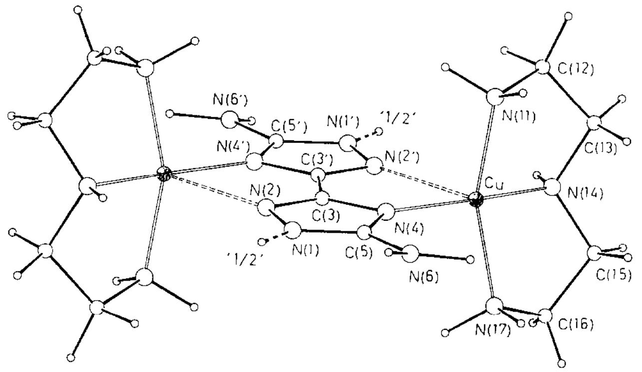


Fig. 1. View of the tripositive cation, with the atomic numbering scheme, in the [{Cu(dien)}$_2$Hdabt](ClO$_4$)$_3$ compound.

of the two Cu atoms of the cation. The high value of the Cu–O(2) and Cu′–O(2′) distances (2.804(17) Å) prevent any true coordination of the two metal centers to the two anions. However, the oxygen atoms of the anions are involved in hydrogen bonding to the exocyclic amine groups of the central bridging ligand and with the dien primary amine nitrogen atoms from neighboring dinuclear complexes. The third perchlorate ion is statistically distributed between two positions related by a crystallographic center of symmetry.

The Cu,N(11),N(14),N(17) part of the cation is roughly co-planar with the two dien ligands which are almost perpendicular to the central plane. This plane is formed by the bridging ligand which is the monoanion of H$_2$dabt. The original asymmetry in this ligand, introduced by the loss of one H$^+$, has disappeared. This is attributable to the static disorder of the remaining active hydrogen atom which is statistically distributed over the two remaining free hydrazinic nitrogen donors. From this point of view the ligand differs from the bridging 2,2′-bis-imidazole [10] which is in its di-anionic state.

Another detail of the structure concerns the CNH$_2$ moieties of Hdabt$^-$ which are completely flattened with the two amino substituents almost coplanar with the triazole rings. This suggests an sp^2 character of the exocyclic amino nitrogen atoms from Hdabt. That they are involved in a conjugated system together with the

Table 3
Selected bond distances (Å) and bond angles (°) of [{Cu(dien)}$_2$Hdabt](ClO$_4$)$_3$ with e.s.d.s in parentheses

(i) In the coordination sphere of the Cu atom			
Cu–N(4)	1.983(11)	Cu–N(17)	1.984(15)
Cu–N(14)	1.977(18)	Cu–N(2)	2.595(13)
Cu–N(11)	2.007(12)		
N(4)–Cu–N(2^{i})	76.8(4)	N(11)–Cu–N(14)	84.4(7)
N(4)–Cu–N(14)	168.6(7)	N(17)–Cu–N(4)	93.7(6)
N(14)–Cu–N(2^{i})	92.4(7)	N(17)–Cu–N(2^{i})	109.1(5)
N(11)–Cu–N(4)	99.1(5)	N(17)–Cu–N(14)	86.5(7)
N(11)–Cu–N(2^{i})	91.3(4)	N(11)–Cu–N(17)	158.0(5)
(ii) In the organic ligands			
N(11)–C(12)	1.50(2)	N(1)–N(2)	1.39(2)
C(12)–C(13)	1.45(3)	N(2)–C(3)	1.28(2)
C(13)–N(14)	1.41(3)	C(3)–N(4)	1.38(2)
N(14)–C(15)	1.46(3)	C(3)–C(3^{i})	1.45(2)
C(15)–C(16)	1.45(4)	N(4)–C(5)	1.33(2)
C(16)–N(17)	1.51(3)	C(5)–N(6)	1.35(2)
N(1)–C(5)	1.35(2)		
N(2)–N(1)–C(5)	105.4(12)	N(4)–C(5)–N(6)	124.0(14)
N(1)–N(2)–C(3)	105.8(12)	N(1)–C(5)–C(6)	123.4(14)
N(1)–N(2)–Cu	154.2(9)	Cu–N(11)–C(12)	107.2(10)
C(3)–N(2)–Cu	100.0(9)	N(11)–C(12)–C(13)	109.7(15)
N(2)–C(3)–N(4)	114.4(13)	C(12)–C(13)–N(14)	109.5(18)
N(2)–C(3)–C(3^{i})	124.5(14)	C(13)–N(14)–C(15)	117.2(17)
N(4)–C(3)–C(3^{i})	121.2(13)	C(13)–N(14)–Cu	110.6(13)
C(3)–N(4)–C(5)	101.8(11)	C(15)–N(14)–Cu	110.3(16)
C(3)–N(4)–Cu	117.6(9)	N(14)–C(15)–C(16)	107.8(18)
C(5)–N(4)–Cu	140.6(9)	C(15)–C(16)–N(17)	113.2(17)
N(4)–C(5)–N(1)	112.6(12)	C(16)–N(17)–Cu	105.5(14)
(iii) Hydrogen bonds			
N(6)···O(2)	3.16(2)	N(6)–H(16)–O(2)	146(8)
H(16)···O(2)	2.10(11)		
N(6)···O(3^{ii})	3.21(2)	N(6)–H(26)–O(3^{ii})	134(8)
H(26)···O(3^{ii})	2.30(11)		
N(11)···O(4^{iii})	2.95(3)	N(11)–H(211)–O(4^{iii})	153(9)
H(211)···O(4^{iii})	1.95(13)		
N(17)···O(1^{iv})	3.08(2)	N(17)–H(117)–O(1^{iv})	148(8)
H(117)···O(1^{iv})	2.11(13)		

Symmetry codes: $^{i}1-x, -y, 1-z$; $^{ii}\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; $^{iii}-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; $^{iv}\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$.

bis-triazole portion is further indicated by the rather short exocyclic C–N distance (1.35 Å) which is in good agreement with the average value (1.355 Å) reported for C_{ar}–NH_2 (Nsp^2) fragments [11].

The coordinating dien ligand is in its common *mer* configuration and the bond lengths and angles of the ligand and its chelate rings with copper are in agreement with those found for many other copper–dien compounds [12].

4. Supplementary material

A list of atomic coordinates, anisotropic thermal parameters, a full list of bond distances and angles and a table of structure factors are available from the authors on request.

Acknowledgements

This work was sponsored by the Leiden Materials Science Centre (Werkgroep Fundamenteel Materialenonderzoek). The present investigations were carried out with financial support from C.N.R. and MURST, Rome, and from the Netherlands Foundation for Chemical Research (SON) through project 333-17.

References

[1] S. Ferrer, J.G. Haasnoot, J. Reedijk, E. Muller, M. Biagini-Cingi, A.M. Manotti-Lanfredi, F. Ugozzoli and C. Foglia, *J. Chem. Soc., Dalton Trans.*, (1992) 3029.

[2] M. Biagini-Cingi, M. Lanfranchi, A.M. Manotti-Lanfredi, S. Ferrer, J.G. Haasnoot and J. Reedijk, *Inorg. Chim. Acta, 209* (1993) 219.

[3] M. Biagini-Cingi, A.M. Manotti-Lanfredi, F. Ugozzoli, J.G. Haasnoot and J. Reedijk, *Gazz. Chim. Ital.*, submitted for publication.

[4] R.N. Shreve and R.K. Charlesworth, *US Patent No. 2 744 116* (1956).

[5] M.S. Lehmann and F.K. Larsen, *Acta Crystallogr., Sect. A, 30* (1974) 580.

[6] F. Ugozzoli, *Comput. Chem., 11* (1987) 109.

[7] G.M. Sheldrick, *SHELX76*, programs for crystal structure determination, University of Cambridge, UK, 1976; *SHELX86*, Institut für Anorganische Chemie der Universität, Göttingen, Germany, 1986.

[8] *International Tables for X-Ray Crystallography*, Vol. 4, Kynoch, Birmingham, UK, 1974.

[9] M. Nardelli, *Comput. Chem., 7* (1983) 95.

[10] M.S. Haddad, E.N. Duesler and D.N. Hendrickson, *Inorg. Chem., 18* (1979) 141.

[11] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. II*, (1987) S1–S19.

[12] T. Sorrell, L.G. Marzilli and T.J. Kistenmacher, *J. Am. Chem. Soc., 98* (1976) 2181.