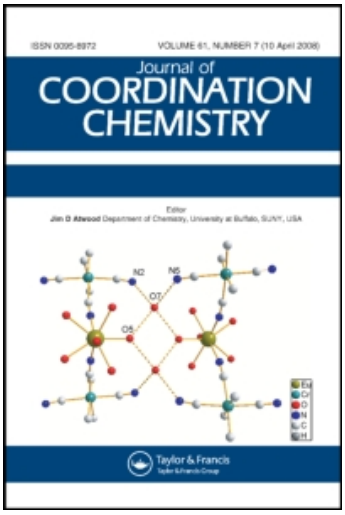

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

CRYSTAL STRUCTURE AND SPECTROSCOPIC PROPERTIES OF DINITRATO-*BIS*(2-METHYLBENZIMIDAZOLE)COPPER(II) METHANOL

Gerard A. Van Albada[a]; Wilberth J. J. Smeets[b]; Anthony L. Spek[b]; Jan Reedijk[a]
[a] Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, RA Leiden, The Netherlands
[b] Bijvoet Center for Biomolecular Research, Vakgroep Kristal-en Structuurchemie, Utrecht University, CH Utrecht, The Netherlands

To cite this Article Van Albada, Gerard A. , Smeets, Wilberth J. J. , Spek, Anthony L. and Reedijk, Jan(1999) 'CRYSTAL STRUCTURE AND SPECTROSCOPIC PROPERTIES OF DINITRATO-*BIS*(2-METHYLBENZIMIDAZOLE)COPPER(II) METHANOL', Journal of Coordination Chemistry, 48: 4, 375 — 381
To link to this Article: DOI: 10.1080/00958979908023577
URL: http://dx.doi.org/10.1080/00958979908023577

J. Coord. Chem., 1999, Vol. 48, pp. 375–381
Reprints available directly from the publisher
Photocopying permitted by license only

Note

CRYSTAL STRUCTURE AND SPECTROSCOPIC PROPERTIES OF DINITRATO-*BIS*(2-METHYLBENZIMIDAZOLE)COPPER(II) METHANOL

GERARD A. VAN ALBADA[a], WILBERTH J.J. SMEETS[b], ANTHONY L. SPEK[b] and JAN REEDIJK[a,*]

[a]*Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands;* [b]*Bijvoet Center for Biomolecular Research, Vakgroep Kristal-en Structuurchemie, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*

(Received 16 November 1998)

The X-ray structure of the title compound has been determined together with spectroscopical properties. The structure consists of a monomeric Cu(II) unit and two nitrate anions. The two *bis*(2-methylbenzimidazole) ligands are in *cis* positions.

Keywords: Benzimidazole; copper; X-ray structure

INTRODUCTION

2-Substituted benzimidazoles have interesting and useful biological properties. For example, 2 fluoromethylbenzimidazole derivitives are used as herbicides[1] and as an uncoupler in oxidative phosphorylation,[2] while 2-a-hydroxybenzylbenzimidazole has antiviral activity.[3] The ligand investigated in this paper, 2-methylbenzimidazole (mbi), is useful as a herbicide as well.[4]

* Corresponding author.

Transition metal complexes with the ligand mbi[5] and a crystal structure of diformato*bis*(mbi)copper(II) were reported earlier.[6] In the latter case the mbi ligands were in *trans* positions. The crystal structure of the mbi ligand is also reported in the literature.[7,8] In this paper we reinvestigate and report the crystal structure of dinitrato(mbi)copper(II)(MeOH), a compound in which the ligands are in *cis* positions and with didentate nitrogen anions.

EXPERIMENTAL

Preparation

Syntheses of the ligand and the complexes were reported earlier;[5] however in this case crystallisation was from methanol instead of ethanol. On standing, blue crystals were formed with the formula $Cu(mbi)_2(NO_3)_2(CH_3OH)$. Yield: 63%. *Anal.* Calcd. for $CuC_{17}H_{20}N_6O_7$ (%): C, 42.19; N, 17.37; H, 4.17; Cu, 13.13. Found: C, 42.05; H, 4.15; N, 17.12; Cu, 12.64.

Physical and Analytical Measurements

C, H, N and Cu determinations were performed by the Microanalytical Laboratory of University College, Dublin, Ireland. Electronic spectra were obtained on a Perkin-Elmer 330 spectrophotometer using the diffuse reflectance technique, with MgO as a reference. X-band powder EPR spectra were obtained on a Jeol RE2x electron spin resonance spectrometer using DPPH ($g = 2.0036$) as a standard.

Crystal Structure Determination

Crystal data are collected in Table I. A blue crystal suitable for X-ray structure determination was covered by an inert oil, glued to the tip of a glass fibre and immediately placed in a cold dinitrogen stream (150 K) on an Enraf-Nonius CAD4-T diffractometer with rotating anode. Data were collected in $\omega/2\theta$ mode. Reduced cell calculations did not indicate higher lattice symmetry (Lepage).[9] Intensity data were corrected for Lorentz, polarization and absorption effects. The structure was solved by automated direct methods (SHELXS86).[10] Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93).[11] All reflections were considered observed during refinement. Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms were included in the

TABLE I Crystallographic data for $Cu(mbi)_2(NO_3)_2(CH_3OH)$

Crystal data	
Formula	$C_{17}H_{20}CuN_6O_7$
Molecular weight	483.94
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 2)
a (Å)	7.593(1)
b (Å)	9.672(1)
c (Å)	14.840(2)
V (Å^3)	1042.7(2)
Z	2
D_{calc}, (g cm^{-3})	1.541
$F(000)$	498
μ (cm^{-1})	11.0
Crystal size (mm)	0.45 × 0.38 × 0.18
Colour	blue
Data collection	
Temperature (K)	298
θ min, θ max deg	1.42, 27.50
Wavelength (MoKα) Å	0.71073 (graphite monochromator)
Data set (*hkl*)	−9 : 9; −12 : 12; −19 : 19
Total data	8904
Total unique data, R_{int}	4774, 0.0690
Observed data ($I > 2\sigma(I)$)	3243
Refinement	
No. of refined parameters	300
$wR2$[a]	0.0952
R[b]	0.0400
S	0.954
w^{-1}[c]	$\sigma^2(Fo^2) + (0.0524P)^2$
$(\Delta/\sigma)_{av}$, $(\Delta/\sigma)_{max}$	0.000, 0.007
min. and max. resd. dens., e/Å^3	−0.41, 0.50

[a] $wR2 = [\sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)^2]]^{1/2}$.
[b] $R1 = \sum||F_0| - |F_c||/\sum|F_0|$.
[c] $P = (\text{Max}(F_0^2, 0 + 2F_c^2)/3)$.

refinement cycle at calculated positions, riding on their carrier atoms, except for the hydrogen atom of the methanol molecule which was located by difference Fourier systhesis. All geometrical calculations and the ORTEP illustrations were performed with PLATON.[12] Computing was conducted on a DEC5000 cluster.

RESULTS AND DISCUSSION

Crystal Structure

The molecular structure with the atom labelling scheme is shown in Figure 1. Coordinates and equivalent isotropic thermal parameters for the

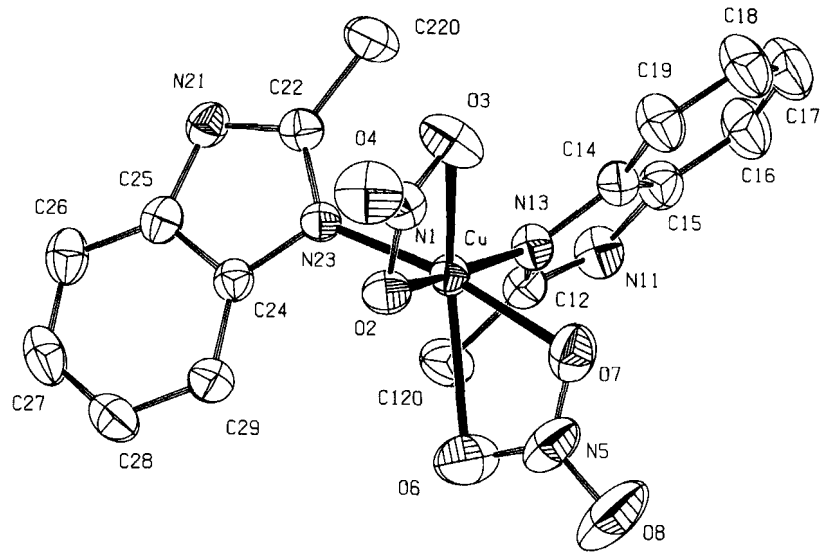

FIGURE 1 ORTEP plot drawn at the 50% probability level with the atom labelling scheme.

non-hydrogen atoms are given in Table II; bond distances and angles are listed in Table III.

The central copper atom is surrounded by two nitrogen atoms from two different mbi ligands. These two ligand are in *cis* positions. The other positions are occupied by four oxygen atoms from two different nitrate anions. The angle of the axial site (O(2)–Cu–N(13) 169.74(11)°) is not quite 180°, which is due to the angles of the nitrate anions (O(2)–Cu–O(3) 55.89(9) and O(6)–Cu–O(7) 56.88(11)°) being the normal angles for didenate coordinated nitrate.[13–15]

Two of the oxygen atoms (one of each nitrate ion) have a semi-coordination bond length (2.415(3) and 2.494(3) Å) given overall a distorted octahedral form. These bond lengths are similar to those found earlier for structures with two didentate coordinated nitrate anions and a CuN_2O_4 chromophore.[13–15]

Cu–N distances are normal as found for imidazole and benzimidazole structures.[16–18] A particular interesting feature of the structure deals with the packing. The structure is stabilized by stacking and hydrogen bonds between the nitrogen anions, the benzimidazole ligand and the methanol molecule. Hydrogen bonds occur between the nitrogen of one mbi ligand and the oxygen of methanol (N(11)···O(9) 2.767(5) Å). The nitrogen of the other mbi ligand forms a hydrogen bond with the oxygen of one of the nitrate-ions (N(21)···O(2) 2.952(4) Å), while the oxygen of the methanol

TABLE II Final coordinates and equivalent isotropic displacement parameters of the non-hydrogen atoms

Atom	*x/a*	*y/b*	*z/c*	$U(eq)/Å^2$
Cu	−0.15808(6)	0.74811(4)	0.28366(3)	0.0302(1)
O2	−0.3579(3)	0.7741(2)	0.40309(16)	0.0383(7)
O3	−0.2122(4)	0.5670(3)	0.4100(2)	0.0585(10)
O4	−0.4341(4)	0.6459(3)	0.52703(19)	0.0636(10)
O6	−0.3436(4)	0.9216(3)	0.2120(2)	0.0639(11)
O7	−0.3572(3)	0.7015(3)	0.22626(18)	0.0504(9)
O8	−0.5308(5)	0.8298(5)	0.1513(2)	0.0940(16)
N1	−0.3361(4)	0.6582(3)	0.4493(2)	0.0390(9)
N5	−0.4130(4)	0.8195(4)	0.1948(2)	0.0533(13)
N11	0.2191(4)	0.6898(3)	0.02900(19)	0.0412(9)
N13	0.0216(4)	0.6901(3)	0.16731(18)	0.0338(8)
N21	0.2645(4)	0.8544(3)	0.38211(18)	0.0344(8)
N23	0.0156(3)	0.8264(3)	0.33810(17)	0.0299(8)
C12	0.1134(5)	0.7676(3)	0.1010(2)	0.0355(10)
C14	0.0690(5)	0.5529(3)	0.1364(2)	0.0353(10)
C15	0.1940(5)	0.5513(4)	0.0494(2)	0.0398(11)
C16	0.2650(6)	0.4284(4)	0.0014(3)	0.0543(14)
C17	0.2067(7)	0.3080(4)	0.0444(3)	0.0615(16)
C18	0.0823(6)	0.3079(4)	0.1311(3)	0.0602(16)
C19	0.0105(6)	0.4299(4)	0.1790(3)	0.0483(11)
C22	0.1719(4)	0.7636(3)	0.3534(2)	0.0320(9)
C24	0.0037(4)	0.9663(3)	0.3592(2)	0.0304(9)
C25	0.1615(4)	0.9858(3)	0.3868(2)	0.0332(9)
C26	0.1895(5)	1.1139(4)	0.4128(2)	0.0428(11)
C27	0.0528(6)	1.2234(4)	0.4124(3)	0.0489(13)
C28	−0.1066(5)	1.2066(4)	0.3861(2)	0.0453(11)
C29	−0.1341(5)	1.0775(3)	0.3589(2)	0.0387(10)
C120	0.1055(5)	0.9226(3)	0.1010(3)	0.0471(11)
C220	0.2405(5)	0.6118(4)	0.3434(3)	0.0486(13)
O9	0.6067(6)	0.2022(4)	0.1415(3)	0.0987(14)
C10	0.5187(9)	0.2936(7)	0.2130(4)	0.095(2)

$U(eq) = 1/3$ of the trace of the orthogonalized U tensor.

TABLE III Bond distances (Angstroms) and angles (Degrees)

Cu–O2	2.018(2)	Cu–O3	2.495(3)
Cu–O6	2.415(3)	Cu–O7	2.027(3)
Cu–N13	1.959(3)	Cu–N23	1.964(3)
O2–Cu–O3	55.88(9)	O2–Cu–O6	87.96(9)
O2–Cu–O7	85.68(10)	O2–Cu–N13	169.74(11)
O2–Cu–N23	91.91(10)	O3–Cu–O6	136.94(10)
O3–Cu–O7	94.32(11)	O3–Cu–N13	116.60(11)
O3–Cu–N23	92.13(11)	O6–Cu–O7	56.88(11)
O6–Cu–N13	95.52(11)	O6–Cu–N23	113.63(11)
O7–Cu–N13	88.13(12)	O7–Cu–N23	170.24(12)
N1–Cu–N23	95.51(12)		

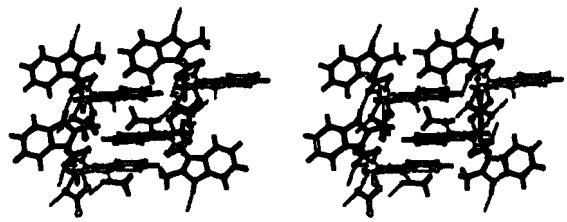

FIGURE 2 Stereo plot of the structure showing the H-bond system.

molecule forms a hydrogen bond with one of the oxygen atoms of a nitrate ion (O(9)···O(6) 2.866(5) Å). Important stacking between the benzimidazole moities of different molecules is observed (Ring–Ring distance of 3.604 Å). The hydrogen-bonding system and the packing are shown in stereo in Figure 2. Cu–O distances of the nitrate ions are in agreement with other didentate nitrate anions from the literature.[13–15]

Infrared Spectroscopy

The characteristic nitrate vibrations are observed as three strong absorptions with centres around 1485, 1385 and 1290 cm^{-1}, consistent with two unsymmetrical nitrate anions.[19]

Electronic Spectroscopy

The diffuse reflectance spectrum of the powdered solid shows a very broad and split band at 13.7 and 16.3 $\times$ 10^3 cm^{-1}, normal for distorted octahedral copper(II) compounds.[20] X-band EPR spectra of the polycrystalline powder were recorded at room temperature. The spectrum shows an axial $S = 1/2$ signal with a $g_\perp$ of 2.08 and an unresolved $g_\parallel$ value of 2.48. These g values are normal values for copper in a distorted octahedral environment.[20] Both results confirm results in the literature.[5]

Supplementary Material

Tables of atomic coordinates, bond lengths and angles of all atoms, thermal parameters, and tables of calculated and observed structure factors are available as supplementary material and may be obtained from one of the authors (A.L.S).

Acknowledgements

This work was supported in part (W.J.J.S and A.L.S) by the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (NWO). The work described in the present paper has been supported by the Leiden University Study group WFMO (Werkgroep Fundamenteel Materialen Onderzoek). Use of the services and facilities of the Dutch National NWO/SURF Expertise Center CAOS/CAMM, under grant numbers SON 326-052 and STW NCH99.1751, is gratefully acknowledged. Dr. J.G. Haasnoot is thanked for his helpful discussions.

References

[1] D.E. Burton, A.H. Lambie, J.C.L. Ludgate, G.T. Newbold, A. Percival and D.T. Saggers, *Nature*, **208**, 1166 (1965).
[2] O.T.G. Jones and W.A. Watson, *Nature*, **208**, 1169 (1965).
[3] A.C. Hollinshead and P.K. Smith, *J. Pharm. Exp. Therapeutics*, **123**, 54 (1958).
[4] U.S. Borax & Chemical Corp., *British Patent*, 1,015,937 (1966).
[5] D.M.L. Goodgame, M. Goodgame and G.W. Rayner-Canham, *Inorg. Chim. Acta*, **6**, 245 (1972).
[6] T.S. Schilperoort, F.J. Rietmeijer, R.A.G. de Graaff and J. Reedijk, *Acta Cryst.*, **C42**, 1491 (1986).
[7] G.L. Starova, V.S. Fundamenskii, V.A. Lopyrev and V.V. Makarskii, *Sov. Phys. Crystallogr.*, **36**, 884 (1991).
[8] A.E. Obodovskaya, Z.A. Starikova, S.N. Belous and I.E. Pokrovskaya, *Structural Chem. USSR*, **32**, 421 (1991).
[9] A.L. Spek, *J. Appl. Crystallogr.*, **21**, 578 (1988).
[10] G.M. Sheldrick, SHELXS-86, Program for crystal structure determination, (University of Göttingen, Germany, 1986).
[11] G.M. Sheldrick, SHELXL-93, Program for crystal structure refinement, (University of Göttingen, Germany, 1993).
[12] A.L. Spek, *Acta Crystallogr.*, **A46**, C34 (1990).
[13] X. Solans, M. Font-Altaba, M. Izquierdo and J. Casabo, *Acta Cryst.*, **C41**, 46 (1985).
[14] D.L. Lewis and D.J. Hodgson, *Inorg. Chem.*, **12**, 1682 (1973).
[15] A.F. Cameron, D.W. Taylor and R.H. Nuttall, *J. Chem. Soc., Dalton Trans.*, 58 (1972).
[16] E. Bouwman, W.L. Driessen and J. Reedijk, *Coord. Chem. Reviews*, **104**, 143 (1990).
[17] G.A. van Albada, M.T. Lakin, N. Veldman, A.L. Spek and J. Reedijk, *Inorg. Chem.*, **34**, 4910 (1995).
[18] G.A. van Albada, W.J.J. Smeets, A.L. Spek and J. Reedijk, *Inorg. Chim. Acta*, **260**, 151 (1997).
[19] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, (John Wiley & Sons, New York, 1986).
[20] B.J. Hathaway, in G. Wilkinson, R.D. Gillard and J.A. McCleverty (Eds.), *Comprehensive Coordination Chemistry*, Vol. 5 (Pergamon, Oxford, 1987).