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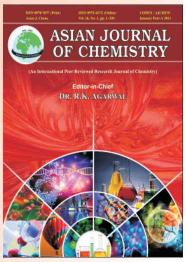

Synthesis, Characterization and X-Ray Crystal Structure of Copper Complex with 18-Crown-6

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A 1:1 crystal of 18-crown-6 with copper has been obtained by stirring and refluxing equimolar quantities of methanolic solution of 18-crown-6 and $Cu(NO_3)_2$ overnight. Cu-18-crown-6 complex is a crystalline solid of blue colour. The complex crystallizes in the monoclinic space group P 2 1/n, with unit cell parameters a = 10.0228(7) Å, b = 12.9341(9) Å, c = 16.7351(12)Å, α = 90.00, β = 92.089(1), γ = 90.00, Z = 4, V = 2168.0 (3) Å3. Copper metal does not fit into the cavity of 18-crown-6, because the cavity size of the 18-crown-6 is bigger than the size of the copper atom. So copper metal is coordinated by water molecule and that water molecules are further connected with 18-crown-6 through hydrogenbonding between water coordinated with copper metal and oxygen atoms of the crown ether. The complex was characterized by using single crystal X-ray spectroscopy, TGA, UV-spectroscopy, IR-spectroscopy and atomic absorption spectroscopy.

Keywords: Crystal, 18-Crown-6, Copper, Single crystal X-Ray.

INTRODUCTION

Association of heteroatom containing macrocyclic compounds such as crown ethers with metal complexes provides a new approach for generation of supramolecular architecture. Intermolecular interactions between metal complexes and crown ethers leading to the formation of associates offer the possibility for design of different metal-containing supramolecular materials and selective extraction of coordination compounds into hydrophobic media[1].

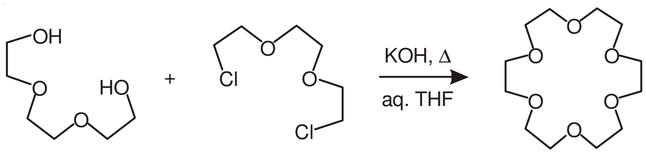
A large amount of crown ether associations have been produced and studied by different methods[2-7]. Most of these species exhibit 1D array structure with the equimolar complex to crown ether stoichiometry. Supramolecular organization determined hydrogen bonding between an oxygen atom of the crown ether and acidic hydrogen(s) of a ligand. Our interest in the oxime chemistry[8-11] and, in particular, in supramolecular aggregations involving metal-bound oximes[12], motivated us to synthesize the complexes of 18-crown-6 with different metals.

The selectivity of the complexation is dependent on many parameters and one of them is size of the cavity. We have been interested in determining the effects of changing the size of the metal atom by making complexes of 18-crown-6 with nickel, copper and zinc. In this paper we report the synthesis, characterization of copper metal complex with 18-crown-6 and trying to show the effect of size of central metal in complex formation.

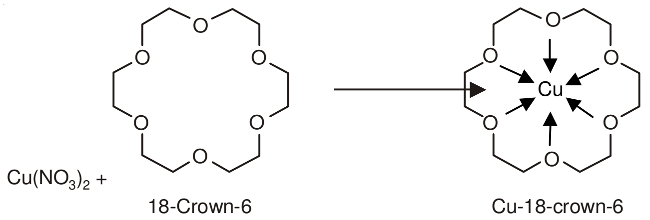
EXPERIMENTAL

Synthesis of 18-crown-6: 22.5 g, (20.1 mL) of triethylene glycol and 120 mL of tetrahydrofuran were reflexed in three-necked flask. 60 % Potassium hydroxide solution, prepared by dissolving 21.8 g. (0.389 mol) of potassium hydroxide in 14 mL. of water, was added. After about 15 min of vigorous stirring, a solution of 28 g of 1,2-*bis*(2-chloroethoxy) ethane in 20 mL of tetrahydrofuran was added in a stream. After the addition is complete, the solution was heated at reflux and stirred vigorously for 18-24 h. After cooling the solution, THF was evaporated and the resulting thick, brown slurry was diluted with 100 mL of dichloromethane and filtered through a glass frit. The salts removed by filtration were washed with more dichloromethane to remove absorbed crown ether and the combined organic solution was dried over anhydrous magnesium sulfate, filtered, evaporated to minimum volume and distilled under high vacuum using a simple vacuum distillation pump. A typical fraction contains 14-17 g. (38-44 %) of crude 18-crown-6.

Purification of crude 18-crown-6: To 10 g of the crude 18-crown-6, 20 mL of acetonitrile was added. The resulting slurry was heated on a hot plate to effect solution. The solution was stirred vigorously as it was allowed to cool to ambient temperature. Fine white crystals of crown-acetonitrile complex were deposited. The flask was allowed to stand in a freezer for 24-48 h to precipitate as much of the complex as possible. The solid was collected by rapid filtration and washed once with a small amount of cold acetonitrile. The hygroscopic crystals were transferred to a 200 mL, round-bottomed flask equipped with a magnetic stirring bar and a vacuum takeoff. Acetonitrile was removed from the complex under high vacuum (using vacuum distillation pump), with gentle heating (35 °C), over 2-3 h. The pure colourless 18-crown-6 (5-7 g, 56-66 %) crystallizes on standing, m.p. 38° C.



Synthesis of Cu-18-crown-6 complex: The reaction was carried out in 1:1 molar ratio. A methanolic solution of copper(II) nitrate was added to a solution of 18-crown-6 in methanol while stirring. The contents were stirred continuously and refluxed overnight and left for a week. The resultant solid product was filtered off and washed with methanol and dried in vacuum.



RESULTS AND DISCUSSION

Copper complex of 18-crown-6 has been synthesized by stirring equimolar quantity of methanolic solution of copper nitrate and 18-crown-6 under reflux overnight. Blue crystals of 1:1 copper complex were obtained by slow evaporation of the solvent. The crystals of copper complex with 18-crown-6 grows in monoclinic space group P 2 1/n, with unit cell parameters a = 10.0228(7) Å , b = 12.9341(9) Å , c = 16.7351 (12) Å , a = 90.00, β = 92.089 (1), γ = 90.00, Z = 4, V = 2168.0 (3) Å3. Fig. 1 shows that unit cell has Z value equal to 4. It means unit cell contains four molecules of the complex. Single crystal of copper complex of 18-crown-6 make a network in three dimensions as shown in Fig. 2. In this complex, copper has coordination number 5 and it is bounded by coordination bond with three molecules of water and two molecules of nitrate. In one dimension, these three water molecules are further attached through hydrogen bonding with oxygen atoms of 18-crown-6 while oxygen atoms of nitrate makes hydrogen bonding with hydrogen atoms attached with carbon atoms of the crown ether in other two dimensions. As we already know that sodium and potassium occupy the centre of the 18-crown-6 but in case of copper metal, copper metal does not occupy the centre of the 18-crown-6 because the size of the sodium or potassium is bigger than copper and copper does not exactly fit into the cavity of the 18-crown-6. The geometry around copper atom is trigonal bipyramidal. In fact copper does not make any direct contact with 18-crown-6 but oxygen atom of three molecules of water and two molecule of nitrate coordinated with copper, further make hydrogen bonding with oxygen and carbon atoms of 18-crown-6. Each coordination sphere is sandwiched between two molecules of 18-crown-6. O7 of water molecule coordinated with copper, makes hydrogen bonding with O6 of one molecule of 18-crown-6 and O3 of other molecule of 18-crown-6. Similarly, O8 and O9 are coordinated with copper at 180° with each other. O8 makes hydrogen bonding with O2 and O4 of one molecule of 18-crown-6 and O9 of the other coordination sphere. Similarly, O9 makes hydrogen bonding with O1, O5 and O6 of the other molecule of 18-crown-6. There are also hydrogen bonds between oxygen atoms of the nitrate and carbon atoms of the 18-crown-6 but these interactions are in other two dimensions *e.i.* C3 makes hydrogen bond with O10 and O11 of nitrate, C6 makes hydrogenbond with O12, C9 makes hydrogen bond with O10^{ii} and O11^{iii}, C10 makes hydrogen bond with O11^{iii} and

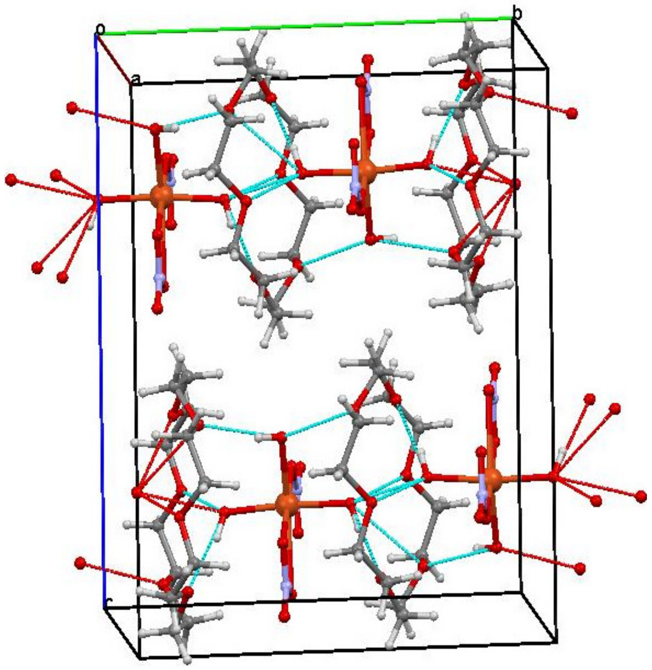


Fig. 1

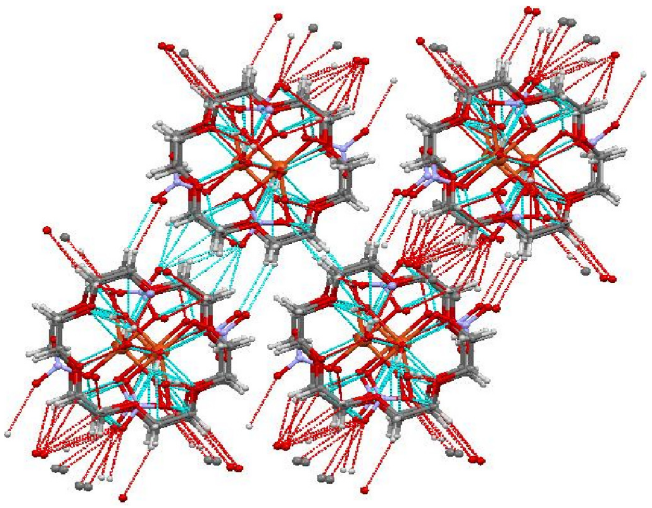


Fig. 2

C12 makes hydrogenbond with $O12^{ii}$ and $O12^{iv}$,. Symmetry transformations used to generate equivalent atoms are (i) -x + 3/2, y + 1/2, -z + 3/2; (ii) -x + 3/2, y-1/2, -z + 3/2; (iii) x + 1/2, -y + 1/2, z-1/2; (iv) x-1/2, -y + 1/2, z-1/2.

Atomic absorption was taken on a Hitachi Z-8000 Polarized Zeeman atomic absorption spectrophotometer. Atomic absorption was done on lamp current 7.5 mA, wavelength 324.8 nm, Slit 1.3 nm, standard burner atomizer. Air was used as an oxidant with oxidant pressure 1.60 Kg/cm^2 and Acetylene as a fuel with fuel pressure 0.30 Kg/cm^2. Burner height was 7.5 mm and flame was used for atomization. The amount of copper estimated by atomic absorption spectroscopy is 8.9 ppm while the calculated one is 10 ppm.

From UV studies, it was concluded that the complex was pure and stable in solid as well as in solution form because the same λ_{max} was achieved even after five weeks. From Fig. 3-5, it is clear that there is no any change in λ_{max} even after five weeks.

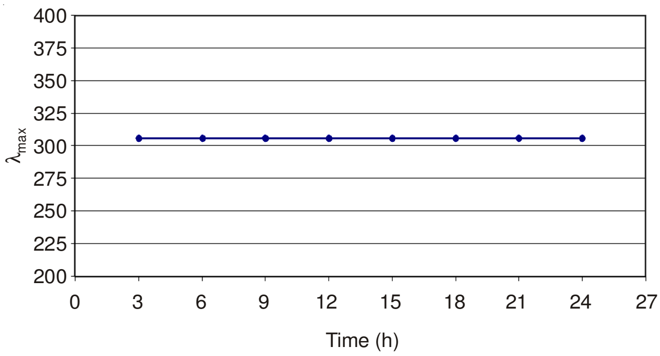


Fig. 3. Graph between λ_{max} *versus* time (h)

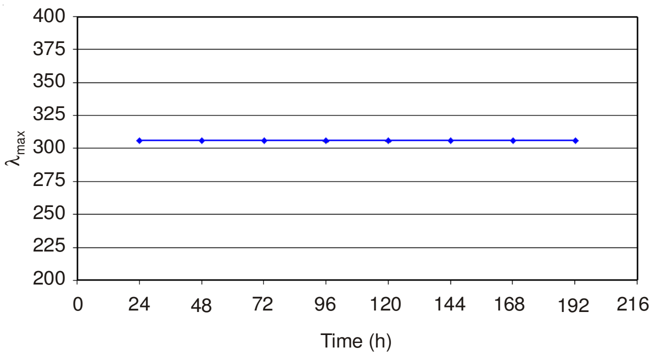


Fig. 4. Graph between λ_{max} *versus* Time (h)

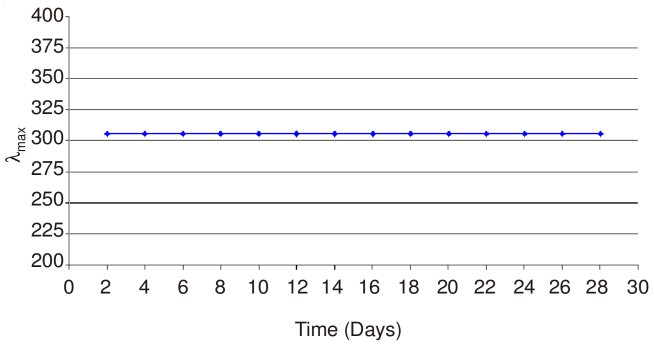


Fig. 5. Graph between λ_{max} *versus* Days

In TGA, we observed the weight loss with respect to increase in temperature for the synthesized copper complexes of 18-crown-6. Graph in Fig. 6 shows that the 1st loss in weight occurs at 101.9 to 170 °C and this loss is 29.16 % and second loss in weight occurs at 170 to 280 °C and this loss is 28.12 %. Total loss in weight from 101.9 to 496 °C is 57.29 %.

IR scan of copper complex with 18-crown-6 (Fig. 7) shows the peaks at 3786, 3697.8, 3658.2, 3377.9, 2922.3, 2853.7 (C-H stretching), 1725.0, 1586.7, 1460.3 (C-H bending), 1375.8 (C-O-C), 1101.6, 957.4, 835.6, 794.7, 723.3 cm^{-1}.

Symmetry transformations used to generate equivalent atoms: (i) -x + 3/2, y + 1/2, -z + 3/2; (ii) -x + 3/2, y-1/2, -z + 3/2; (iii) x + 1/2, -y + 1/2, z-1/2; (iv) x-1/2, -y + 1/2, z-1/2.

Stability determination of copper complex of 18-crown-6: (a) λ_{max} of Cu complex of 18-crown-6 solution in H_2O was determined while it was synthesized. (λ_{max} = 306 nm).

(b) The above solution was kept for five weeks and its λ_{max} was periodically noted as following and a graph of λ_{max} was plotted against time.

1. After every 3 h for first 24 h (Fig. 3).
2. After 24 h for first week (Fig. 4).
3. After 48 h (2 days) for rest of the 5 weeks (Fig. 5).

No change was noted through out the experiment. Every time a fresh solution was also run for λ_{max} to check its stability in solid crystalline form and there was also no change in λ_{max} in the fresh solution.

TGA of synthesized complex of copper with 18-crown-6: In TGA we observed the weight loss with respect to increase in temperature for the synthesized copper complexes of 18-crown-6.

Graph in Fig. 6 shows that the 1st loss in weight occurs at 101.9 to 170 °C and this loss is 29.16 % and second loss in weight occurs at 170 to 280 °C and this loss is 28.12 %. Total loss in weight from 101.9 to 496 °C is 57.29 %.

There is no peak in melting point region. Hence it is concluded that the metal complex is stable, which is also supported by UV studies.

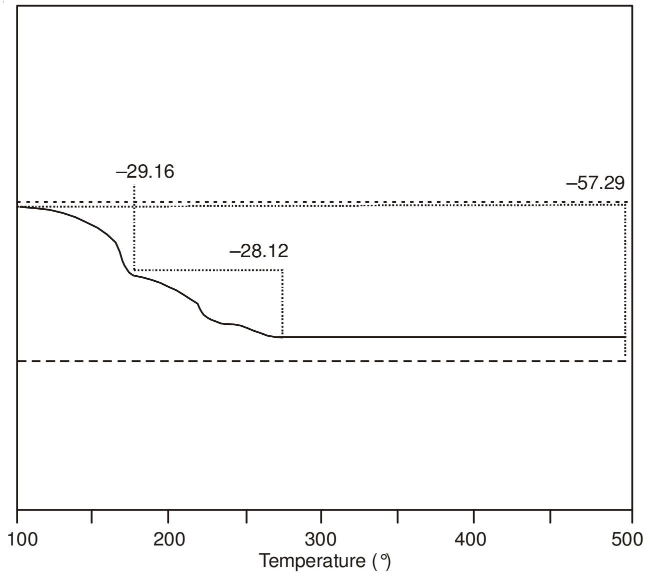


Fig. 6. TGA graph of Cu-18-crown-6 complex

IR-Spectroscopic studies of copper complex of 18-crown-6

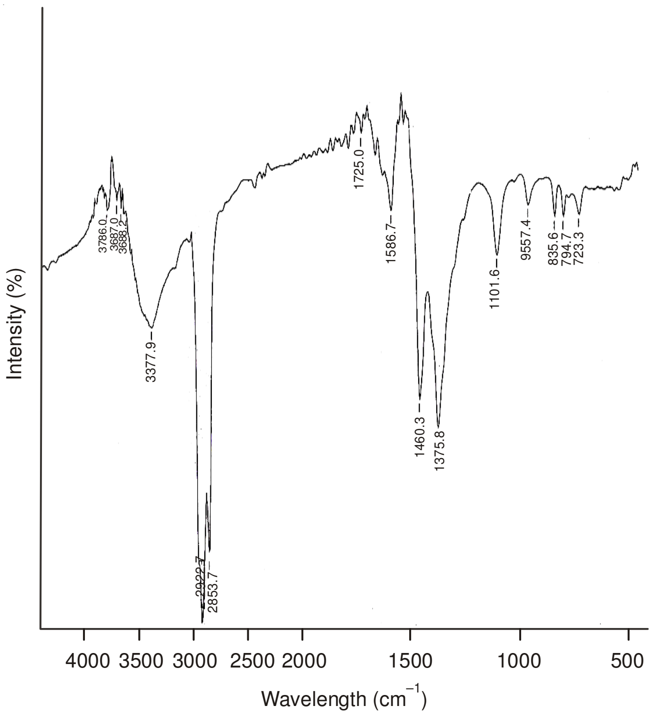


Fig. 7. IR-Scan of copper complex of 18-crown-6

Conclusion

Copper complex of 18-crown-6 shows that coordination number of copper is 5 and copper is bounded by coordination bond with three molecules of water and two molecules of nitrate. These three water molecules and oxygen atoms of nitrate further makes hydrogen bonding with oxygen atoms of 18-crown-6 and hydrogen atoms attached with carbon atoms of 18-crown-6 crown. As the size of copper metal is smaller than the cavity of the 18-crown-6, so copper metal does not occupy the centre of the 18-crown-6. This complex shows trigonal bipyramidal geometry around copper atom. The copper amount measured by atomic absorption spectroscopy is 8.9 ppm while the calculated one is 10 ppm. UV and TGA studies show that complex was pure and stable in solid as well as in solution form as the λ_{max} was same even after five weeks and no peak was obtained in melting point region in TGA.

Single-crystal X-ray analysis: Structure Determination and Refinement was carried out on a Bruker Smart Apex II diffractometer using MoK$_\alpha$ radiation (k = 0.71073 A °). The APEX2[13,14] program package was used for cell refinements and data reductions. The structure was solved by direct methods using SHELXL-2012[15] with the WinGX[16] graphical user interface. An empirical absorption correction (SADABS)[17] was applied to the data. Structural refinements were carried out using SHELXL-97[18,19]. All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters and hydrogen atoms bonded to carbon were inserted at calculated positions and hydrogen atoms bonded to carbon were inserted at calculated positions using a riding model. Crystallographic data is shown in Tables 1-5.

TABLE-1
CRYSTAL DATA

$C_{12}H_{27}N_2O_{15}Cu$	Z = 4
M_r = 502.89	F(000) = 1048
Monoclinic, $P2_1/n$	D_x = 1.541 Mg m^{-3}
a = 10.0228 (7) Å	MoKα radiation, λ = 0.71073 Å
b = 12.9341 (9) Å	μ = 1.08 mm^{-1}
c = 16.7351 (12) Å	T = 150 K
β = 92.089 (1)°	0.35 × 0.14 × 0.10 mm
V = 2168.0 (3) Å^3	

TABLE-2
DATA COLLECTION

Absorption correction: multi-scan	R_{int} = 0.040
T_{min} = 0.703, T_{max} = 0.904	θ_{max} = 28.4°, θ_{min} = 2.0°
22015 measured reflections	h = -130 → 13
5422 independent reflections	k = -17→ 17
3811 reflections with I > 2σ(I)	l = -21 → 22

TABLE-3
REFINEMENT

Refinement on F^2	0 restraints
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.036	H-atom parameters constrained
$wR(F^2)$ = 0.098	$w = 1/[\sigma^2(F_o^2) + (0.0452P)^2 + 0.8353P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.04	$(\Delta/\sigma)_{max}$ = 0.009
5422 reflections	$\Delta >_{max}$ = 0.73 e Å^{-3}
274 parameters	$\Delta >_{min}$ = -0.35 e Å^{-3}

TABLE-4
GEOMETRIC PARAMETERS (Å, °)

Cu1-O8	1.9602 (15)	O3-C7	1.425 (3)
Cu1-O9	1.9616 (15)	O3-C6	1.426 (3)
Cu1-O13	1.9672 (15)	O4-C8	1.429 (3)
Cu1-O10	1.9905 (15)	O4-C9	1.435 (3)
Cu1-O7	2.2480 (15)	O5-C11	1.426 (3)
N1-O11	1.226 (2)	O5-C10	1.431 (3)
N1-O12	1.241 (3)	O6-C12	1.426 (3)
N1-O10	1.300 (2)	O6-C1	1.429 (3)
N2-O14	1.227 (3)	C1-C2	1.493 (4)
N2-O15	1.232 (3)	C3-C4	1.492 (4)
N2-O13	1.297 (2)	C5-C6	1.493 (4)
O1-C2	1.424 (3)	C7-C8	1.496 (3)
O1-C3	1.430 (3)	C9-C10	1.496 (4)
O2-C5	1.425 (3)	C11-C12	1.499 (4)
O2-C4	1.436 (3)		
O8-Cu1-O9	174.45 (6)	C7-O3-C6	113.05 (18)
O8-Cu1-O13	92.52 (6)	C8-O4-C9	111.67 (18)
O9-Cu1-O13	91.47 (7)	C11-O5-C10	110.98 (19)
O8-Cu1-O10	87.13 (6)	C12-O6-C1	112.6 (2)
O9-Cu1-O10	88.92 (6)	N1-O10-Cu1	106.98 (12)
O13-Cu1-O10	179.28 (6)	N2-O13-Cu1	114.79 (13)
O8-Cu1-O7	94.00 (6)	O6-C1-C2	108.9 (2)
O9-Cu1-O7	90.05 (6)	O1-C2-C1	108.6 (2)
O13-Cu1-O7	87.04 (6)	O1-C3-C4	110.2 (2)
O10-Cu1-O7	92.35 (6)	O2-C4-C3	110.0 (2)
O11-N1-O12	124.0 (2)	O2-C5-C6	109.75 (9)
O11-N1-O10	118.8 (2)	O3-C6-C5	109.0 (2)
O12-N1-O10	117.25 (7)	O3-C7-C8	108.97 (19)
O14-N2-O15	123.5 (2)	O4-C8-C7	108.52 (9)
O14-N2-O13	118.90 (8)	O4-C9-C10	109.79 (9)
O15-N2-O13	117.6 (2)	O5-C10-C9	110.6 (2)

C2-O1-C3	112.1 (2)	O5-C11-C12	109.5 (2)
C5-O2-C4	110.46 (9)	O6-C12-C11	109.1 (2)
O11-N1-O10-Cu1	179.98 (7)	C7-O3-C6-C5	176.11 (9)
O12-N1-O10-Cu1	-0.2 (2)	O2-C5-C6-O3	-68.9 (2)
O14-N2-O13-Cu1	1.3 (3)	C6-O3-C7-C8	-164.89(9)
O15-N2-O13-Cu1	-178.97(7)	C9-O4-C8-C7	178.15 (9)
C12-O6-C1-C2	165.2 (2)	O3-C7-C8-O4	72.9 (2)
C3-O1-C2-C1	-178.4 (2)	C8-O4-C9-C10	173.28 (9)
O6-C1-C2-O1	-71.5 (3)	C11-O5-C10-C9	-169.0 (2)
C2-O1-C3-C4	-170.4 (2)	O4-C9-C10-O5	-69.3 (3)
C5-O2-C4-C3	167.4 (2)	C10-O5-C11-C12	-174.6 (2)
O1-C3-C4-O2	70.6 (3)	C1-O6-C12-C11	-179.2 (2)
C4-O2-C5-C6	174.7 (2)	O5-C11-C12-O6	67.0 (3)

TABLE-5
HYDROGEN-BOND GEOMETRY (Å)

D-H···A	D-H	H···A	D···A	D-H···A
O7-H7···O6	0.84	1.99	2.803 (2)	162
O8-H8···O2	0.84	2.10	2.925 (2)	169
O9-H9···O5^{i}	0.84	2.02	2.849 (2)	168
O9-H9···O6^{i}	0.84	2.62	3.028 (2)	111
C3-H3B···O10	0.99	2.55	3.360 (3)	139
C3-H3B···O11	0.99	2.62	3.453 (3)	141
C6-H6A···O12	0.99	2.54	3.452 (3)	152
C9-H9A···O10^{ii}	0.99	2.47	3.300 (3)	141
C12-H12B···O12^{ii}	0.99	2.50	3.387 (3)	150
C9-H9B···O11^{iii}	0.99	2.50	3.191 (3)	126
C10-H10B···O11^{iii}	0.99	2.53	3.133 (3)	119
C12-H12A···O12^{iv}	0.99	2.30	3.212 (3)	154

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REFERENCES

1. Batinic-Haberle and A.L. Crumbliss, *Inorg. Chem.*, **34**, 928 (1995).
2. H.M. Colquhoun, D.F. Lewis, J.F. Stoddart and D.J. Williams, *J. Chem. Soc., Dalton Trans*., 607 (1983).
3. H.M. Colquhoun, J.F. Stoddart and D.J. Williams, *J. Chem. Soc. Chem. Commun*., 851 (1981).
4. H.M. Colquhoun, J.F. Stoddart, D.J. Williams, J.B. Wolstenholme and R. Zarzycki, *Angew. Chem. Int. Ed. Engl*., **20**, 1051 (1981).
5. P.A. Cusack, B.N. Patel, P.J. Smith, D.W. Allen and I.W. Nowell, *J. Chem. Soc., Dalton Trans*., 1239 (1984).
6. I. Ando, M. Higashi, K. Ujimoto and H. Kurihara, *Inorg. Chim. Acta*, **282**, 247 (1998).
7. T.G. Chulkova, P.V. Gushchin, M. Haukka and V.Yu. Kukushkin, *Inorg. Chem. Commun*., **13**, 580 (2010).
8. V.Yu. Kukushkin, D. Tudela and A.J.L. Pombeiro, *Coord. Chem. Rev*., **156**, 333 (1996).
9. V.Yu. Kukushkin and A.J.L. Pombeiro, *Coord. Chem. Rev*., **181**, 147 (1999).
10. M.N. Kopylovich, V.Yu. Kukushkin, M. Haukka, K.V. Luzyanin and A.J.L. Pombeiro, *J. Am. Chem. Soc*., **126**, 15040 (2004).
11. K.V. Luzyanin, V.Yu. Kukushkin, M.L. Kuznetsov, D.A. Garnovskii, M. Haukka and A.J.L. Pombeiro, *Inorg. Chem*., **41**, 2981 (2002).
12. V.Yu. Kukushkin, T. Nishioka, D. Tudela, K. Isobe and I. Kinoshita, *Inorg. Chem*., **36**, 6157 (1997).
13. V.Yu. Kukushkin, D. Tudela, Y.A. Izotova, V.K. Belsky and A.I. Stash, *Polyhedron*, **17**, 2455 (1998).
14. Bruker, APEX2, GIS, SADABS and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA (2009).
15. G.M. Sheldrick, *Acta Crystallogr. A*, **64**, 112 (2008).
16. L.J. Farrugia, *J. Appl. Cryst*., **32**, 837 (1999).
17. G.M. Sheldrick, SADABS-Bruker AXS Scaling and Absorption Correction, Bruker AXS Inc., Madison (2008).
18. K. Brandenburg, Diamond-Crystal and Molecular Structure Visualization, v. 3.2g. Crystal Impact GbR, Bonn (2011).
19. J.D. Dunitz, P. Seiler and R.P. Phizackerley, *Acta Crystallogr. B*, **30**, 2739 (1974).