Acta Chemica Scandinavica A 39 (1985) 475–481

The Structure of an Oxamido-bridged Cu(II)-Dimer: $[(Et_5dien)\text{-}Cu(C_2H_2N_2O_2)Cu(Et_5dien)](PF_6)_2$

JORUNN SLETTEN

Department of Chemistry, University of Bergen, Realfagbygget, N-5000 Bergen, Norway

The structure of $[(Et_5dien)Cu(oa)Cu(Et_5dien)](PF_6)_2$, where "$Et_5dien$" is *N,N,N',N'',N''*-pentaethyldiethylenetriamine and "oa" is the oxamido dianion, has been determined by X-ray crystallographic methods. The crystals are monoclinic, space group $P2_1/n$, with cell dimensions a=8.474(6) Å, b=20.697(19) Å, c=12.112(9) Å, β=97.92(6)°; Z=2. Diffractometer data were collected at approximately 140 K. The structure was solved by direct methods and refined to an R of 0.035 using 1779 observed reflections. The complex consists of centrosymmetric oxamido-bridged binuclear cations, the anions being uncoordinated. The Cu-ions are 5-coordinated with a coordination geometry intermediate between square pyrimidal and trigonal bipyramidal. Cu–N distances to Et_5dien are 2.382(4). 2.024(4), 2.092(4) Å; to oa 1.940(4) Å; and Cu–O is 2.030(3) Å. Judged from the coordination geometry a significant antiferromagnetic interaction would be expected for this compound.

This investigation is part of a study of structures of binuclear (or polynuclear) complexes in which the metal ions may be magnetically coupled through polyatomic bridging groups. Previously structure determinations of two oxamido-bridged,[1] two oxalato-bridged,[2] and one carbonato-bridged[3] Cu-complexes have been reported in this series. Molecular orbital models aimed at explaining the exchange mechanism through extended bridges have been put forward and discussed.[4–6] And various attempts at correlating coordination geometry and magnetic properties have been done.[7–12] However, still additional data is needed to obtain a more detailed knowledge of the relationship between the parameters involved in determining the degree of magnetic exchange through polyatomic bridges.

EXPERIMENTAL

The compound was synthesized by Nonoyama *et. al.*[13] Green prismatic crystals suitable for X-ray investigation were grown from ethanol by slow evaporation at room temperature. The crystal used had dimensions 0.11×0.12×0.22mm. Cell dimensions were determined and intensity data were recorded at 140K on a CAD-4 diffractometer using monochromatized Mo$K\alpha$-radiation. ω-scan was employed with scan widths $\Delta\omega$=1.5+0.35 tanθ, and scan speed 4°/min. Three reference reflections were remeasured at regular intervals during data collection: the data were corrected in accordance with the slight deterioration observed. All together 2772 independent reflections were recorded up to 2θ=45°.

0302-4377/85 $2.50

CRYSTAL DATA

[μ-Oxamido-bis{*N*,*N*,*N'*,*N''*,*N''*-pentaethyldiethylenetriaminecopper(II)}] phosphorhexafluoride; $Cu_2C_{30}H_{68}F_{12}N_8O_2P_2$; monoclinic, $P2_1/n$ (No 14); a=8.474(6) Å, b=20.697(19) Å, c=12.112(9) Å, β=97.92(6)°, V=2104(3)Å^3 (at 140 K), M=989.94, Z=2, D_x=1.56 g cm^{-3}, μ=11.78 cm^{-1}.

STRUCTURE DETERMINATION AND REFINEMENT

The structure was determined by direct methods. In the E-map Cu, the bridging group and the PF_6-moiety were found. The remaining non-hydrogen atoms were localized in subsequent Fourier maps; hydrogen atoms were localized in a difference map. The structure was refined using full-matrix least-squares methods. For non-hydrogen atoms anisotropic thermal parameters were used, for hydrogen atoms isotropic ones. For some of the hydrogen atoms B-values became negative. These were reset to a positive value, and during the final least-squares cycles thermal parameters on hydrogen atoms were held fixed. The weight assigned to each reflection in the refinement is $w=[\sigma_F^2+(0.01F_o)^2]^{-1}$ where σ_F=

Table 1a. Final coordinates and isotropic equivalent thermal parameter (defined as $B_{eq}=\frac{4}{3}\sum_i\sum_j \beta_{ij}a_i\cdot a_j$) for anisotropically refined atoms.

Atom	x	y	z	B_{eq}(Å^2)
Cu	0.40044(7)	0.41050(3)	0.35085(5)	1.02(1)
P	0.6887(2)	0.65559(6)	0.1904(1)	1.36(3)
F1	0.5433(3)	0.6649(1)	0.0942(2)	2.40(7)
F2	0.8345(4)	0.6473(2)	0.2870(2)	3.27(8)
F3	0.6934(3)	0.7317(1)	0.2121(2)	2.24(7)
F4	0.6842(4)	0.5799(1)	0.1684(2)	2.93(7)
F5	0.8104(3)	0.6634(1)	0.1016(2)	2.48(7)
F6	0.5664(4)	0.6483(1)	0.2783(2)	2.93(7)
O	0.4290(4)	0.5201(1)	0.6246(2)	1.05(7)
N0	0.3584(4)	0.4393(2)	0.4965(3)	1.07(9)
N1	0.2197(4)	0.4777(2)	0.2344(3)	1.15(9)
N2	0.4743(4)	0.3855(2)	0.2047(3)	0.86(8)
N3	0.3467(4)	0.3127(2)	0.3686(3)	0.99(9)
C1	0.4392(5)	0.4889(2)	0.5365(4)	0.9(1)
C2	0.0481(6)	0.4741(2)	0.2456(4)	1.5(1)
C3	0.0052(6)	0.5025(3)	0.3518(4)	1.9(1)
C4	0.2790(6)	0.5450(2)	0.2499(4)	1.4(1)
C5	0.1862(6)	0.5961(3)	0.1779(4)	2.2(1)
C6	0.2452(6)	0.4531(2)	0.1247(4)	1.4(1)
C7	0.4163(6)	0.4343(2)	0.1189(4)	1.4(1)
C8	0.6539(5)	0.3809(2)	0.2182(4)	1.3(1)
C9	0.7242(6)	0.3555(3)	0.1188(4)	2.2(1)
C10	0.4004(6)	0.3214(2)	0.1765(4)	1.3(1)
C11	0.4196(6)	0.2801(2)	0.2782(4)	1.3(1)
C12	0.4214(6)	0.2871(2)	0.4788(4)	1.5(1)
C13	0.5963(6)	0.3049(3)	0.5085(4)	2.0(1)
C14	0.1725(6)	0.2976(2)	0.3542(4)	1.6(1)
C15	0.0734(6)	0.3297(2)	0.4328(4)	1.8(1)

Table 1b. Final atomic parameters for hydrogen atoms. Thermal parameters are defined by $\exp[-B\sin^2\theta/\lambda^2]$.

Atom	x	y	z	B (Å^2)
H01	0.309(4)	0.424(2)	0.530(3)	1
H21	−0.025(5)	0.494(2)	0.176(3)	1
H22	0.019(4)	0.433(2)	0.245(3)	0
H31	−0.105(5)	0.489(2)	0.356(3)	0
H32	0.064(5)	0.488(2)	0.421(3)	2
H33	0.021(6)	0.549(2)	0.365(4)	4
H41	0.386(5)	0.547(2)	0.231(3)	1
H42	0.280(4)	0.554(2)	0.331(3)	0
H51	0.067(6)	0.606(2)	0.200(4)	5
H52	0.159(4)	0.585(2)	0.107(3)	0
H53	0.247(5)	0.637(2)	0.184(3)	2
H61	0.218(4)	0.488(2)	0.067(3)	0
H62	0.178(4)	0.421(2)	0.105(3)	0
H71	0.484(4)	0.469(2)	0.134(3)	0
H72	0.431(4)	0.421(2)	0.044(3)	1
H81	0.687(4)	0.357(2)	0.280(3)	1
H82	0.697(4)	0.417(2)	0.240(3)	0
H91	0.836(4)	0.362(2)	0.139(3)	0
H92	0.696(5)	0.381(2)	0.052(3)	2
H93	0.703(5)	0.310(2)	0.105(4)	2
H101	0.443(4)	0.301(2)	0.118(3)	1
H102	0.300(5)	0.329(2)	0.148(3)	2
H111	0.370(4)	0.240(2)	0.259(3)	0
H112	0.534(4)	0.271(2)	0.306(3)	1
H121	0.363(5)	0.307(2)	0.531(3)	1
H122	0.403(5)	0.241(2)	0.481(4)	3
H131	0.624(5)	0.297(2)	0.576(3)	1
H132	0.617(5)	0.351(2)	0.508(3)	1
H133	0.673(5)	0.285(2)	0.454(3)	2
H141	0.170(5)	0.250(2)	0.358(4)	3
H142	0.122(5)	0.307(2)	0.286(3)	2
H151	0.075(4)	0.376(2)	0.425(3)	0
H152	0.108(5)	0.317(2)	0.512(4)	2
H153	−0.046(5)	0.311(2)	0.408(4)	3

$\sigma_c(I\,Lp)^{-\frac{1}{2}}$. Of the 2772 independent reflections in the data set 1779 had $|F_o| > 3\sigma_F$, and these were included in the refinement. The refinement converged at $R=0.035$, $R_w=0.026$, and a standard deviation of an observation of unit weight of 1.30.

Atomic scattering factors used were those of Cromer and Waber.[14] All calculations were carried out on a PDP 11/55 computer using the Enraf-Nonius Structure Determination Programs (SDP).[15]

Atomic parameters are listed in Table 1a and b. An ORTEP drawing of the binuclear cation (Fig. 1) shows the atomic numbering used: and the crystal packing is shown in Fig. 2. Bond distances and angles are listed in Tables 2 and 3, respectively.

Lists of structure factors and of anisotropic thermal parameters may be obtained from the author.

Table 2. Bond distances(Å). Numbers in parentheses are estimated standard deviations in the last significant digits.[a]

Atom1	Atom2	Distance	Atom1	Atom2	Distance	Atom1	Atom2	Distance
Cu	O^i	2.030(3)	P	F6	1.592(3)	N3	C12	1.494(6)
Cu	N0	1.940(4)	O	C1	1.261(5)	N3	C14	1.496(6)
Cu	N1	2.382(4)	N0	C1	1.291(6)	C1	$C1^i$	1.517(8)
Cu	N2	2.024(4)	N1	C2	1.481(6)	C2	C3	1.503(7)
Cu	N3	2.092(4)	N1	C4	1.484(6)	C4	C5	1.519(7)
P	F1	1.587(3)	N1	C6	1.466(6)	C6	C7	1.512(7)
P	F2	1.589(3)	N2	C7	1.484(5)	C8	C9	1.509(7)
P	F3	1.597(3)	N2	C8	1.510(5)	C10	C11	1.491(7)
P	F4	1.588(3)	N2	C10	1.486(6)	C12	C13	1.521(7)
P	F5	1.597(3)	N3	C11	1.491(6)	C14	C15	1.508(7)
N0	H01	0.70(4)	C6	H62	0.88(4)	C12	H121	0.95(4)
C2	H21	1.05(4)	C7	H71	0.91(4)	C12	H122	0.97(5)
C2	H22	0.88(4)	C7	H72	0.98(4)	C13	H131	0.84(4)
C3	H31	0.98(4)	C8	H81	0.91(4)	C13	H132	0.96(4)
C3	H32	0.96(4)	C8	H82	0.86(4)	C13	H133	1.07(4)
C3	H33	0.99(5)	C9	H91	0.96(4)	C14	H141	0.99(5)
C4	H41	0.96(4)	C9	H92	0.97(4)	C14	H142	0.90(4)
C4	H42	0.99(4)	C9	H93	0.96(5)	C15	H151	0.96(4)
C5	H51	1.10(5)	C10	H101	0.94(4)	C15	H152	1.00(5)
C5	H52	0.89(4)	C10	H102	0.89(4)	C15	H153	1.09(5)
C5	H53	0.99(4)	C11	H111	0.94(4)			
C6	H61	1.00(4)	C11	H112	1.00(4)			

[a] i: $1-x$, $1-y$, $1-z$.

Table 3. Bond angles(°) not involving hydrogen atoms. Numbers in parentheses are estimated standard deviations.[a]

At.1	At.2	At.3	Angle	At.1	At.2	At.3	Angle	At.1	At.2	At.3	Angle
O^i	Cu	N0	82.3(1)	F3	P	F4	179.8(2)	C8	N2	C10	110.8(4)
O^i	Cu	N1	93.5(1)	F3	P	F5	90.5(2)	Cu	N3	C11	104.2(3)
O^i	Cu	N2	90.5(1)	F3	P	F6	89.3(2)	Cu	N3	C12	111.3(3)
O^i	Cu	N3	146.1(1)	F4	P	F5	89.4(2)	Cu	N3	C14	114.6(3)
N0	Cu	N1	100.1(2)	F4	P	F6	90.9(2)	C11	N3	C12	109.2(4)
N0	Cu	N2	172.2(2)	F5	P	F6	179.5(2)	C11	N3	C14	108.7(4)
N0	Cu	N3	97.7(2)	Cu	O	C1	110.8(3)	C12	N3	C14	108.7(4)
N1	Cu	N2	83.3(1)	Cu	N0	C1	115.5(3)	O	C1	N0	129.0(4)
N1	Cu	N3	119.6(1)	Cu	N1	C2	118.4(3)	O	C1	$C1^i$	118.0(5)
N2	Cu	N3	86.6(1)	Cu	N1	C4	107.1(3)	N0	C1	$C1^i$	112.9(5)
F1	P	F2	179.2(2)	Cu	N1	C6	99.8(3)	N1	C2	C3	114.5(4)
F1	P	F3	90.0(2)	C2	N1	C4	110.8(4)	N1	C4	C5	116.2(4)
F1	P	F4	89.9(2)	C2	N1	C6	109.6(4)	N1	C6	C7	113.2(4)
F1	P	F5	90.1(2)	C4	N1	C6	110.5(4)	N2	C7	C6	111.7(4)
F1	P	F6	89.5(2)	Cu	N2	C7	109.0(3)	N2	C8	C9	116.0(4)
F2	P	F3	89.2(2)	Cu	N2	C8	110.5(3)	N2	C10	C11	109.1(4)
F2	P	F4	90.9(2)	Cu	N2	C10	105.0(3)	N3	C11	C10	109.7(4)
F2	P	F5	89.9(2)	C7	N2	C8	110.5(4)	N3	C12	C13	113.9(4)
F2	P	F6	90.5(2)	C7	N2	C10	111.0(4)	N3	C14	C15	117.4(4)

[a] i: $1-x$, $1-y$, $1-z$.

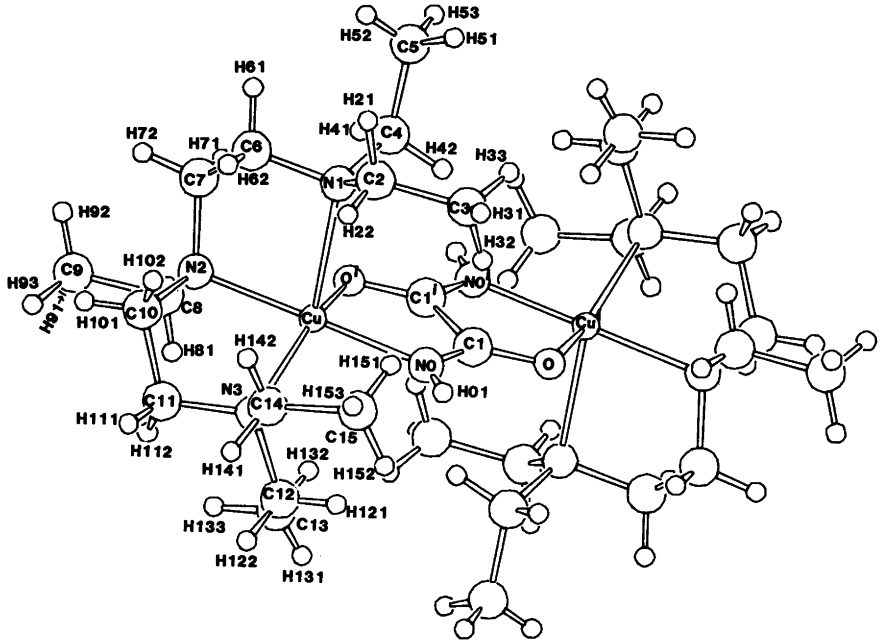

Fig. 1. The dimeric unit of $[(Et_5dien)Cu(oa)Cu(Et_5dien)]^{2+}$

RESULTS AND DISCUSSION

The complex cation consists of dimeric units in which two metal ions are centrosymmetrically bridged by an oxamido group, the outer ligands being Et_5dien. PF_6^- -ions do not bind to copper (Figs. 1 and 2). The Cu-ion is 5-coordinated with a coordination geometry intermediate between square pyramidal (SP) and trigonal bipyramidal (TBP) (Fig. 1, Tables

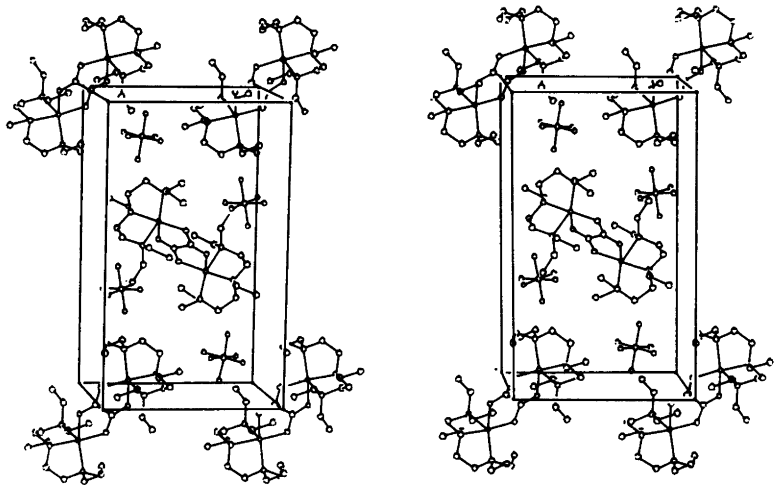

Fig. 2. Crystal packing as viewed approximately down the *a*-axis. The origin of the unit cell is in the upper left hand corner, with *b* running top to bottom and *c* left to right.

2, 3). In the SP description the oxamido O and N atoms and N2, N3 of Et_5dien constitute the equatorial plane, with the third Et_5dien nitrogen, N1, in the apical position. The equatorial ligand atoms deviate by −0.27, +0.26, +0.25, −0.24 Å, respectively, from the best least-squares plane, and Cu is displaced by +0.34Å towards the apical ligand. In the TBP description, on the other hand, the oxygen and the the terminal Et_5dien nitrogens, N1, N3 constitute the equtorial plane. Cu is displaced by 0.10 Å from this plane towards N0.

The coordination geometry caused by Et_5dien as outer ligand in a bridged complex has been found to be intermediate between SP and TBP, but with somewhat varying degree of distortion. For instance, when comparing the present complex with that of the analogous oxalato bridged complex $[(Et_5dien)Cu(ox)Cu(Et_5dien)](PF_6)_2$,[2] it is seen that although in both cases the geometry is intermediate between SP and TBP, the oxamido group occupies two equatorial positions, while the oxalato group occupies one axial and one equatorial position. In a closely related compound, $[(Et_5dienCu(ox)Cu(Et_5dien)](BPh_4)_2$,[8] the geometry is appreciably closer to TBP than in the two former examples. And, finally, in the unsymmetrical complex, $[Cu(oxpn)Cu(Et_5dien)](ClO_4)_2$,[16] the coordination geometry on the Et_5dien side is very close to that observed in the present compound.

The oxamido-bridged complex reported here has a subnormal room temperature magnetic moment (μ=1.42 B.M.), while the equivalent oxalato-bridged complex, has a normal room temperature magnetic moment (1.82 B.M.).[13,2] In this latter case temperature dependent magnetic susceptibilities and EPR-measurements have shown that antiferromagnetic interaction is present to a certain extent ($J=-9.6$ cm^{-1}).[8] No corresponding measurements are available for the present compound; − only the μ-value cited above may indicate a higher degree of antiferromagnetic coupling when the bridge is an oxamido-group. A similar trend in μ-values has also been observed for other pairs of analogous oxalato- and oxamido-bridged Cu-dimers.[13,17] It has been suggested that the reason for the enhanced exchange through an oxamido- as compared to an oxalato group, is that the magnetic orbital is more delocalized towards a less electronegative bridging N-atom than towards an O-atom.[18,16]

In addition to this effect, any change in Cu-coordination geometry may influence the degree of magnetic exchange. In the idealized case of a pure SP geometry with two equatorial positions on Cu for the bridging oxalato or oxamido ligand (SP_{ee}) the magnetic orbitals ($d_{x^2-y^2}$) on the two centrosymmetrically related Cu-ions would both be located in the plane of the bridging group, and a large antiferromagentic interaction would be expected.[6,8,16,17] An SP geometry with one axial and one equatorial position for the bridging group (SP_{ae}) would result in magnetic orbitals on Cu being normal to the plane of the bridging moiety. In this case a small interaction would be expected. TBP geometry would give intermediate interaction. As mentioned above, the present structure is closer to the SP_{ee} geometry, the analogous oxalato compound is closer to the SP_{ae} geometry. This difference in geometry may be partly responsible for the apparent change in magnetic interaction.

Acknowledgement. Thanks are due to Professor M. Nonoyama for supplying a sample of the compound.

REFERENCES

1. Sletten, J. *Acta Chem. Scand. A 36* (1982) 345.
2. Sletten, J. *Acta Chem. Scand. A 37* (1983) 569.
3. Sletten, J. *Acta Chem. Scand. A 38* (1984) 491.

4. Hay, P.J., Thibeault, J.C. and Hoffman, R. *J. Am. Chem. Soc. 97* (1975) 4884.
5. Kahn, O. and Briat, B. *J. Chem. Soc. Faraday Trans. 2* (1976) 268, 1441.
6. Kahn, O. and Charlot, M.F. *Nouv. J. Chim. 4* (1980) 567.
7. Hall, G.R., Duggan, D.M. and Hendrickson, D.N. *Inorg. Chem. 14* (1975) 1956.
8. Felthouse, T.R., Laskowski, E.J. and Hendrickson, D.N. *Inorg. Chem. 16* (1977) 1077.
9. Pierpont, C.G., Francesconi, L.C. and Hendrickson, D.N. *Inorg. Chem. 16* (1977) 2367.
10. Girerd, J.J., Jeannin, S., Jeannin, Y. and Kahn, O. *Inorg. Chem. 17* (1978) 3034.
11. Girerd, J.J., Kahn, O. and Verdaguer, M. *Inorg. Chem. 19* (1980) 274.
12. Julve, M., Verdaguer, M., Kahn, O., Gleizes, A. and Philoche-Levisalles, M. *Inorg. Chem. 22* (1983) 368; *Ibid. 23* (1984) 3808.
13. Nonoyama, K., Ojima, H., Ohki, K. and Nonoyama, M. *Inorg. Chim. Acta 41* (1980) 155.
14. Cromer, D.T. and Waber, J.T. *International Tables for X-Ray Crystallography,* Kynoch Press, Birmingham 1974, Vol. 4, p. 99.
15. Frez, B. *The SDP User's Guide,* Enraf-Nonius, Delft 1979.
16. Journaux, Y., Sletten, J. and Kahn, O. *Inorg. Chem.* (1985). *In press.*
17. Nonoyama, M. and Nonoyama, K. *J. Inorg. Nucl. Chem. 43* (1981) 2567.
18. Kahn, O. *Angew. Chem.* (1985). *In press.*

Received March 15, 1985.