Acta Chemica Scandinavica A 37 (1983) 569–578

The Structures of two Oxalato-bridged Cu-Dimers; $[Cu_2(Me_4en)_2(C_2O_4)(H_2O)_2](PF_6)_2 \cdot 2H_2O$ and $[Cu_2(Et_5dien)_2(C_2O_4)](PF_6)_2$

JORUNN SLETTEN

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

The structures of $[Cu_2(Me_4en)_2(C_2O_4)(H_2O)_2](PF_6)_2 \cdot 2H_2O$ and $[Cu_2(Et_5dien)_2(C_2O_4)](PF_6)_2$, where Me_4en is *N,N,N',N'*-tetramethylethylenediamine and Et_5dien is *N,N,N',N'',N''*-pentaethyldiethylenetriamine, have been determined using heavy atom X-ray methods. The Me_4en-compound crystallizes in the triclinic space group $P\bar{1}$ with cell dimensions $a=7.932(5)$ Å, $b=8.117(7)$ Å, $c=12.089(15)$ Å, $\alpha=96.89(9)°$, $\beta=97.03(8)°$, $\gamma=102.44(6)°$, $Z=1$. The structure was refined to an R of 0.053 using 1353 observed reflections. The Et_5dien compound is monoclinic, space group $I2/c$ (conventional setting $C2/c$) with cell dimensions $a=13.436(9)$ Å, $b=22.29(2)$ Å, $c=14.59(1)$ Å, $\beta=103.68(7)°$, $Z=4$, and was refined to an R of 0.045 using 2112 observed reflections. Both compounds are centrosymmetric binuclear complexes bridged by an oxalate group. The Cu-coordination in the Me_4en compound is slightly distorted square pyramidal with the bridging group occupying two equatorial coordination sites and a water molecule in the apex position; while in the Et_5dien compound a geometry intermediate between square pyramidal and trigonal bipyramidal is found; the oxalate oxygen atoms occupying one equatorial and one axial position.

Magnetic exchange interactions in transition metal dimers, and structural properties of such complexes have been studied extensively over the last few years. Much work has been focused on systems with single atom bridges.[1-2] However, metal-metal interaction is also found in dimers containing various polyatomic bridging groups like *e.g.* formate and oxalate, and with geometries such that no short metal-metal contact is present. Attempts have been made to find correlations between magnetic properties and coordination geometry in such complexes.[3-8] The magnetic properties apparently depend upon both the type of bridging ligand and outer ligand involved, the counter ion, as well as the coordination geometry.[3] More data is needed in order to sort out the various factors involved. Recently a series of dimeric Cu and Ni complexes with μ-oxamido, μ-oxamato and μ-oxalato bridges were synthesized by Nonoyama *et al.*[9,10] Most of these complexes have subnormal magnetic moments at room-temperature, indicating metal-metal magnetic interaction. The present paper presents structural data on two of these compounds containing μ-oxalato-bridges. In a previous paper the structures of two complexes with μ-oxamido-bridges were reported.[11]

EXPERIMENTAL

Both compounds were synthesized by Nonoyama *et. al.*[9] Crystals suitable for X-ray investigations grew by slow evaporation from methanol/water solutions at room temperature. The Me_4en complex crystallized as bright blue, tiny platelets which fractured easily and had a high mosaic spread. The crystal used for X-ray measurements was lost at the end of the data collection, hence dimensions were not measured. The Et_5dien complex crystallized as dark blue prisms; dimensions of the crystal used were $0.45\times0.38\times0.24$ mm. Intensity data were collected at 85 K and 140 K, respectively, on a

0302-4377/83 $2.50

Table 1. Measurement of intensity data.

Compound	Me_4en	Et_5dien
Temperature (K)	85	140
Scan type	ω	ω
Scan range (°)	$\Delta\omega$=3.5	$\Delta\omega$=2.0
Scan speed (°/min)	10	60
Max. 2θ (°)	45	45
No. of unique refl. measured	1957	2787
"Observed" refl.	1353	2112
Cutoff	$3\sigma_c$	$2\sigma_c$

Syntex $P2_1$ diffractometer using monochromatized Mo$K\alpha$-radiation. A summary of the data collection parameters is listed in Table 1. The intensities were corrected for Lorentz and polarizations effects; no absorption correction was carried out.

CRYSTAL DATA

Me_4en complex. (μ-oxalato-[bis{aqua-*N,N,N',N'*-tetramethylethylenediaminecopper(II)}]phosphorhexafluoride dihydrate, $Cu_2C_{14}H_{40}F_{12}N_4O_8P_2$, triclinic, $P\bar{1}$ (No2). a=7.932(5) Å, b=8.117(7) Å, c=12.089(15) Å, α=96.89(9)°, β=97.03(8)°, γ=102.44(6)°, V=745.7(1.3) Å^3, M=809.51, Z=1, D_m=1.78 g cm^{-3}, D_x(85K)=1.803 g cm^{-3}, μ(Mo$K\alpha$)=16.51 cm^{-1}.

Et_5dien complex. [μ-oxalato-bis{*N,N,N',N'',N''*-pentaethyldiethylenetriaminecopper(II)}]phosphorhexafluoride, $Cu_2C_{30}H_{66}F_{12}N_6O_4P_2$, monoclinic, *I2/c* (No 15, standard setting *C2/c*). a=13.436(9) Å, b=22.29(2) Å, c=14.59(1) Å, β=103.68(7)°, V=4244(6) Å^3, M=991.91, Z=4, D_m=1.54 g cm^{-3}, D_x(140K)=1.553 g cm^{-3}, μ(Mo$K\alpha$)=11.70 cm^{-1}.

STRUCTURE DETERMINATIONS

Both structures were solved using the heavy atom technique, and refined by least-squares methods. All hydrogen atoms, except one on the water of crystallization in the Me_4en compound, were localized in difference Fourier maps, and were refined isotropically. For non-hydrogen atoms anisotropic thermal parameters were employed. The weight assigned to each reflection in the refinement is $w=[\sigma_F^2+(kF_o)^2]^{-1}$ where $\sigma_F=\sigma_c(I\cdot \mathrm{Lp})^{-1/2}$ and k=0.02. Final R-factors are 0.053 and 0.045 for the Me_4en and Et_5dien complex, respectively. Weighted R-factors are 0.051 and 0.044, and the standard deviations of an observation of unit weight 2.00 and 1.29, respectively.

Atomic scattering factors were taken from International Tables IV.[12] All calculations were carried out on an Eclipse computer employing the SHELXTL program system.[13]

Final atomic parameters are listed in Tables 2 and 3, bond lengths and angles in Tables 4 and 5. Bond distances and angles involving hydrogen atoms are not listed, they are all normal within the limits of errors. C–H bond lengths in the range 0.83–1.11 Å are found in the Me_4en compound and in the range 0.73–1.19 Å in the Et_5dien compound. Standard deviations in these bond lengths are in the range 0.05–0.11 Å. Molecular framework and numbering schemes are shown in Figs. 1 and 2, packing diagrams in Figs. 3 and 4. Lists of observed and calculated structure factors and of anisotropic thermal parameters may be obtained from the author.

RESULTS AND DISCUSSION

Each complex consists of a dimeric unit with two metal ions being bridged centrosymmetri-

Table 2. Final coordinates and equivalent U-values of non-hydrogen atoms with estimated standard deviations in parentheses. Equivalent U-values are defined by: $U_{eq}=1/3\,\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$. Fractional atomic coordinates have been multiplied by a factor of 10^4 and thermal parameters by 10^3, except the parameters of Cu in the Et_5dien compound which have been multiplied by factors of 10^5 and 10^4, respectively.

Atom	x	y	z	U_{eq}
Me_4en compound				
Cu	2450(1)	1329(1)	1722(1)	25(1)
O1	242(7)	1806(7)	1007(5)	28(2)
O2	1870(7)	−670(7)	446(5)	24(2)

Table 2. Continued.

OW1	3876(8)	3190(7)	732(6)	36(3)
OW2	2727(9)	−6031(8)	119(7)	36(3)
N1	4519(9)	611(8)	2481(6)	25(3)
N2	2493(9)	2823(8)	3209(7)	29(3)
C1	−455(11)	715(11)	165(7)	23(3)
C2	5926(11)	621(12)	1782(9)	37(4)
C3	3971(11)	−1177(11)	2746(8)	30(3)
C4	5178(14)	1843(14)	3519(10)	39(4)
C5	3682(13)	2266(12)	4059(9)	40(4)
C6	728(11)	2636(11)	3568(8)	29(3)
C7	3138(12)	4655(11)	3107(10)	35(4)
P	−1233(3)	−2877(3)	2935(2)	29(1)
F1	−1947(6)	−1518(6)	3721(4)	35(2)
F2	−2954(6)	−3211(6)	2039(4)	38(2)
F3	486(6)	−2563(6)	3828(4)	34(2)
F4	−2178(7)	−4391(6)	3560(5)	42(2)
F5	−293(6)	−1368(6)	2306(4)	37(2)
F6	−518(7)	−4232(6)	2143(5)	42(2)
Et_5dien compound				
Cu	16986(5)	6693(3)	49941(4)	246(2)
O1	1085(3)	208(2)	5874(2)	26(1)
O2	288(3)	324(2)	4007(2)	28(1)
N1	2814(3)	8(2)	4955(3)	25(2)
N2	2291(3)	1131(2)	4058(3)	26(2)
N3	1210(3)	1500(2)	5417(3)	30(2)
C1	222(4)	−37(2)	5536(4)	23(2)
C2	3683(4)	56(3)	5825(4)	34(2)
C3	3425(5)	−160(3)	6726(4)	41(2)
C4	2386(4)	−613(2)	4828(4)	31(2)
C5	3165(5)	−1105(3)	4761(4)	40(2)
C6	3212(4)	182(3)	4118(4)	30(2)
C7	3306(4)	856(2)	4072(4)	32(2)
C8	1581(4)	1090(3)	3099(4)	31(2)
C9	1864(4)	1471(3)	2341(4)	36(2)
C10	2396(4)	1765(3)	4413(4)	35(2)
C11	1411(5)	1932(3)	4685(4)	37(2)
C12	1813(4)	1701(3)	6367(4)	43(2)
C13	1641(5)	1351(3)	7195(4)	55(3)
C14	75(4)	1479(2)	5369(4)	33(2)
C15	−405(5)	2083(3)	5519(5)	48(3)
P1	0(0)	2990(1)	2500(0)	30(1)
P2	5000(0)	1537(1)	7500(0)	43(1)
F1	0(0)	2270(2)	2500(0)	36(2)
F2	−567(3)	2988(2)	3349(2)	44(1)
F3	0(0)	3708(2)	2500(0)	54(2)
F4	−1086(2)	2985(1)	1754(2)	41(1)
F5	4216(3)	2042(2)	7636(3)	74(2)
F6	4498(3)	1531(2)	6387(2)	55(1)
F7	4218(3)	1029(2)	7646(3)	67(2)

Table 3. Atomic parameters of hydrogen atoms. Isotropic temperature factors are defined by $\exp[-8\pi^2 U \sin^2 \theta/\lambda^2]$. All values are multiplied by 10^3.

Atom	*x*	*y*	*z*	*U*
Me_4en compound				
H21	682(9)	42(9)	213(6)	17(20)
H22	547(12)	−4(13)	104(8)	58(31)
H23	620(13)	169(13)	163(9)	64(32)
H31	359(8)	−178(8)	196(5)	1(17)
H32	505(9)	−141(9)	326(6)	25(21)
H33	310(10)	−114(10)	318(7)	38(24)
H41	577(12)	146(12)	409(8)	42(29)
H42	592(13)	290(14)	332(9)	66(34)
H51	412(10)	299(10)	483(7)	32(24)
H52	347(12)	131(12)	425(8)	58(29)
H61	79(9)	322(9)	437(6)	19(20)
H62	−3(8)	298(8)	304(5)	3(16)
H63	37(9)	158(10)	361(7)	28(22)
H71	243(11)	498(11)	246(7)	45(26)
H72	448(11)	482(11)	290(8)	43(26)
H73	353(16)	530(16)	391(11)	101(43)
HW11	509(12)	333(11)	51(8)	52(28)
HW12	350(10)	375(10)	50(7)	35(24)
HW21	−209(14)	−572(14)	61(9)	8(41)
Et_5dien compound				
H21	390(4)	49(2)	591(3)	42(15)
H22	427(4)	−15(2)	569(3)	36(15)
H31	404(4)	−7(2)	724(4)	52(17)
H32	338(4)	−54(2)	671(3)	29(14)
H33	283(4)	11(3)	684(4)	64(19)
H41	183(3)	−58(2)	418(3)	20(12)
H42	205(3)	−64(2)	532(3)	15(11)
H51	350(4)	−100(2)	420(3)	36(15)
H52	364(4)	−118(2)	533(3)	35(15)
H53	273(4)	−148(2)	460(4)	52(17)
H61	384(3)	−1(2)	417(2)	0(10)
H62	276(3)	2(2)	355(3)	16(12)
H71	351(3)	93(2)	359(3)	3(10)
H72	386(4)	103(2)	466(3)	39(15)
H81	154(4)	70(2)	288(3)	34(14)
H82	92(4)	117(2)	311(4)	47(16)
H91	249(3)	143(2)	229(3)	14(11)
H92	140(4)	140(2)	171(4)	42(16)
H93	188(4)	188(2)	252(3)	39(15)
H101	253(3)	202(2)	392(3)	25(13)
H102	302(4)	178(2)	501(3)	31(14)
H111	85(4)	191(2)	410(3)	33(14)
H112	150(4)	231(2)	504(3)	42(16)
H121	180(4)	218(2)	658(3)	39(15)
H122	243(5)	161(2)	634(4)	58(18)
H131	159(5)	82(3)	715(4)	84(22)
H132	202(5)	152(2)	771(4)	52(19)
H133	90(5)	138(3)	729(4)	87(20)
H141	3(3)	119(2)	589(3)	5(10)
H142	−23(4)	136(2)	473(4)	56(18)
H151	−31(4)	232(3)	490(4)	68(19)
H152	−95(4)	203(3)	542(4)	55(18)
H153	−12(4)	221(2)	617(4)	51(17)

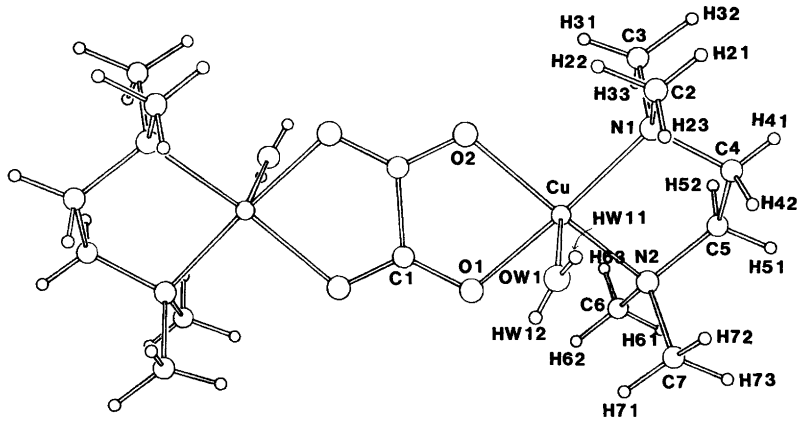

Fig. 1. Dimeric unit of $[Cu_2(Me_4en)_2(C_2O_4)(H_2O)_2]^{2+}$.

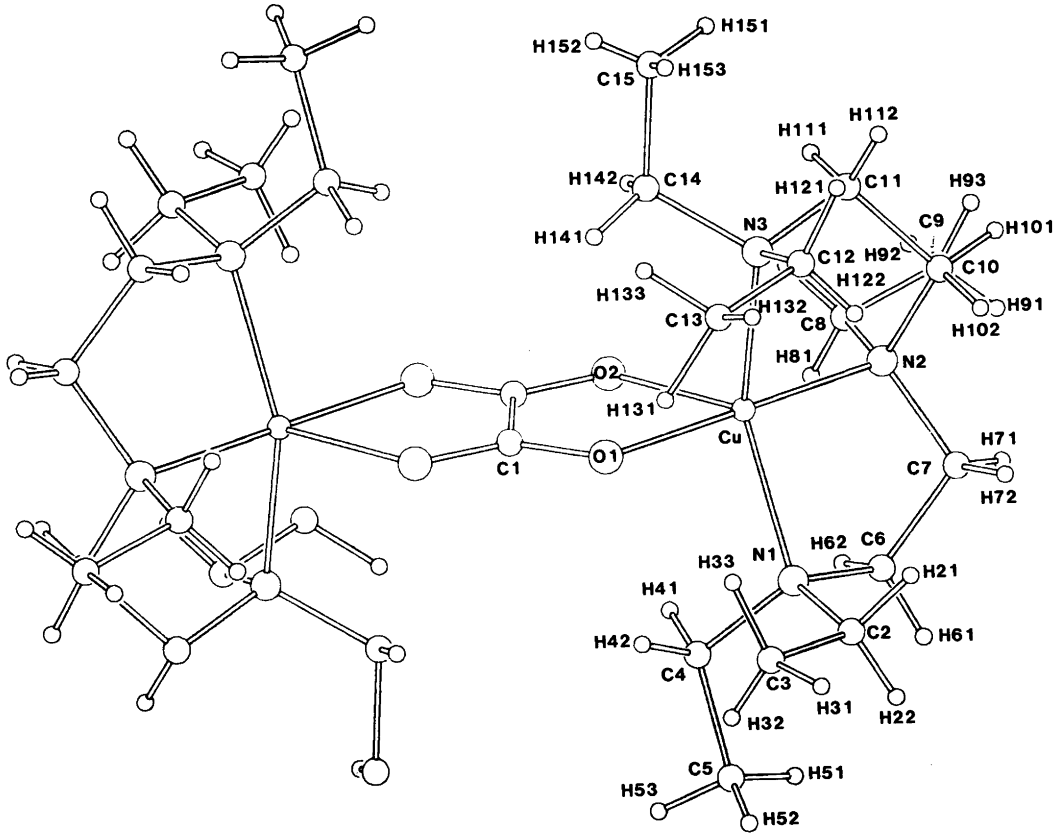

Fig. 2. Dimeric unit of $[Cu_2(Et_5dien)_2(C_2O_4)]^{2+}$.

Table 4. Bond lengths (Å).

Me_4en compound			
Cu–O1	1.992(6)	N1–C2	1.480(13)
Cu–O2	2.032(6)	N1–C3	1.508(11)
Cu–N1	2.011(8)	N1–C4	1.469(13)
Cu–N2	2.037(8)	C4–C5	1.505(16)
Cu–OW1	2.241(7)	N2–C5	1.486(13)
O1–C1	1.249(9)	N2–C6	1.497(12)
O2–C1′	1.257(10)	N2–C7	1.490(11)
C1–C1′	1.533(18)		
Et_5dien compound			
Cu–O1	1.971(4)	C4–C5	1.534(8)
Cu–O2	2.229(4)	C6–C7	1.511(8)
Cu–N1	2.113(5)	N2–C7	1.490(7)
Cu–N2	2.017(5)	N2–C8	1.499(6)
Cu–N3	2.104(5)	N2–C10	1.501(7)
O1–C1	1.271(6)	C8–C9	1.512(9)
O2–C1′	1.241(7)	C10–C11	1.515(9)
C1–C1′	1.545(10)	N3–C11	1.508(8)
N1–C2	1.511(6)	N3–C12	1.500(7)
N1–C4	1.494(7)	N3–C14	1.511(7)
N1–C6	1.495(8)	C12–C13	1.501(9)
C2–C3	1.515(9)	C14–C15	1.529(9)

cally by an oxalate ion (Figs. 1 and 2). The Cu···Cu distances within the dimers are 5.232(4)Å and 5.457(3)Å for the Me_4en and Et_5dien complex, respectively.

The coordination geometry. In the Me_4en compound a somewhat distorted square pyramidal (SP) coordination geometry is found with oxalate and diamine coordinating in the equatorial plane. Cu is displaced 0.208 Å from a best least-squares plane through the equatorial ligand atoms towards the apical water oxygen OW1; while O1, O2, N1, N2 deviate 0.106, −0.105, 0.101, −0.101 Å, respectively, from this plane, showing a significant tetrahedral distortion. The sixth position, opposite to OW1 is blocked by the proximity of F5 of the PF_6-group (see Fig. 3); Cu···F5 being 2.953 Å and ∠F5···Cu − OW1=160.3°. The coordination geometry is similar to that found in a copper dimer containing an oxamido bridge and bipyridyl as outer ligand, $([Cu_2(oa)(bipy)_2](NO_3)_2 \cdot 3H_2O)$,[11] although in the latter case the apical position is occupied by the anion. Both of these compounds are reported to have subnormal magnetic moments at room temperature (1.00 B.M. for the oxamido, 1.47 B.M. for the oxalato bridged dimer),[9] indicating magnetic interaction between metal ions. No study on temperature dependence of the magnetic susceptibility has been done for these two compounds. However, for a structurally closely related SP complex with a dithiooxamide derivative as bridging group equatorially, very strong antiferromagnetic coupling has been shown to be present in two different modifications.[8,17] A mechanism for a σ-type magnetic exchange through the bridging ligand has been proposed for such complexes with SP geometry, $d_{x^2-y^2}$ Cu(II)ion ground state, and the bridging ligand occupying two equatorial coordination sites.[8] Strong antiferromagnetism has also been measured in cases of square planar[6] and elongated octahedral[14] geometry with equatorial oxalate bridges.

In the Et_5dien compound the coordination geometry is intermediate between SP and trigonal bipyramidal (TBP). If regarding the complex as SP, oxalate oxygen O2 occupies the apical position with the other oxalate oxygen atom and the nitrogen atoms in the basal plane. Deviations from a best least-squares plane through O1, N1, N2, N3 are 0.238, −0.251, 0.264, −0.251 Å, respectively; the Cu atom deviating by 0.218 Å towards the axial ligand. The values listed here as well as the bond angles (Table 5) show that the

Table 5. Bond angles (°)

Me_4en compound, copper coordination			
O1–Cu–O2	83.4(2)	O2–Cu–N2	162.3(3)
O1–Cu–N1	173.8(3)	O2–Cu–OW1	94.9(2)
O1–Cu–N2	93.6(3)	N1–Cu–N2	87.2(3)
O1–Cu–OW1	87.6(2)	N1–Cu–OW1	98.3(3)
O2–Cu–N1	93.9(3)	N2–Cu–OW1	102.4(3)
Me_4en compound, oxalate bridge			
Cu–O1–C1	111.1(6)	O1–C1–C1′	118.5(9)
Cu–O2–C1′	111.0(5)	O2–C1–C1′	115.9(8)
O1–C1–O2′	125.6(8)		
Me_4en compound, tetramethylethylenediamine			
Cu–N1–C2	113.2(6)	Cu–N2–C6	113.0(5)
Cu–N1–C3	110.3(5)	Cu–N2–C7	110.0(6)
Cu–N1–C4	105.8(6)	Cu–N2–C5	105.8(6)
C2–N1–C3	107.0(7)	C6–N2–C7	107.2(7)
C2–N1–C4	109.5(7)	C6–N2–C5	109.5(7)
C3–N1–C4	111.0(8)	C7–N2–C5	111.4(6)
N1–C4–C5	110.3(8)	N2–C5–C4	108.9(9)
Et_5dien compound, copper coordination			
O1–Cu–O2	79.5(1)	O2–Cu–N2	98.6(2)
O1–Cu–N1	93.6(2)	O2–Cu–N3	102.5(2)
O1–Cu–N2	178.1(2)	N1–Cu–N2	86.6(2)
O1–Cu–N3	93.5(2)	N1–Cu–N3	153.4(2)
O2–Cu–N1	104.0(2)	N2–Cu–N3	87.2(2)
Et_5dien compound, oxalate bridge			
Cu–O1–C1	117.1(3)	O1–C1–C1′	116.4(6)
Cu–O2–C1′	108.9(3)	O2–C1′–C1	118.0(5)
O1–C1–O2′	125.6(4)		
Et_5dien compound, pentaethyldiethylenetriamine			
Cu–N1–C2	109.9(3)	Cu–N3–C14	110.0(3)
Cu–N1–C4	113.3(3)	Cu–N3–C12	113.3(3)
Cu–N1–C6	103.5(3)	Cu–N3–C11	103.5(3)
C2–N1–C4	111.6(4)	C14–N3–C12	111.8(4)
C2–N1–C6	108.2(4)	C14–N3–C11	109.6(4)
C4–N1–N6	109.9(4)	C12–N3–C11	108.3(4)
N1–C2–C3	114.6(5)	N3–C14–C15	114.9(4)
N1–C4–C5	114.9(5)	N3–C12–C14	115.8(5)
N1–C6–C7	110.3(5)	N3–C11–C10	110.0(4)
C6–C7–N2	108.8(4)	C11–C10–N2	107.8(5)
Cu–N2–C7	106.8(3)	C7–N2–C8	111.5(4)
Cu–N2–C8	109.6(3)	C7–N2–C10	111.8(4)
Cu–N2–C10	105.4(3)	C8–N2–C10	111.5(4)

distortion from idealized SP geometry is appreciable. Viewing the complex as distorted TBP, N1, N3 and O2 define the equatorial plane, with Cu 0.035 Å out of this plane in the direction of O1.

The room temperature magnetic moment of this compound is reported to be normal (1.82 B.M).[9] However, temperature dependent magnetic susceptibilities and EPR measurements have shown that antiferromagnetic interaction is present,[3] although to an appreciably smaller

extent than in the compounds referred to above.[6,8] Felthouse *et al.*[3] have discussed the difference in magnetic exchange mechanisms between dimers with TBP and SP geometry, where the oxalate-type bridge in both cases occupies one axial and one equatorial coordination site. The authors suggest the greatest antiferromagnetic interaction is likely to be found in TBP complexes, with a gradual decrease as the geometry is distorted towards SP. Comparing the present Et_5dien compound with two closely related compounds, $[Cu_2(Et_5dien)_2(C_2O_4)](BPh_4)_2$ and $[Cu_2(dien)_2(C_2O_4)](ClO_4)_2$,[3,15] for which structures as well as magnetic properties are known, we find indeed such a variation. $[Cu_2(Et_5dien)_2(C_2O_4)](BPh_4)_2$ has a geometry fairly close to TBP, and a magnetic exchange parameter of $J = -37.4$ cm^{-1}.[3]

$(Cu_2(dien)_2(C_2O_4)](ClO_4)_2$ approximates SP geometry,[15] and in this case the susceptibility shows no sign of exchange interaction down to 4.2 K ($|J| < \sim 0.5$ cm^{-1}).[3] The present Et_5dien compound with the described intermediate geometry has intermediate magnetic properties as well, $J = -9.6$ cm^{-1}.[3]

From the data referred to in the preceeding paragraphs it appears that the strongest antiferromagnetic interaction is found in the complexes with $d_{x^2-y^2}$ Cu(II) ion ground state (square planar, square pyramidal or elongted octahedral geometry) and the oxalate type bridging group occupying two equatorial sites. Somewhat weaker exchange interaction is present when there is a d_{z^2} Cu(II) ion ground state (TBP geometry) and oxalate is occupying one equatorial and one axial site. The weakest interaction is found in a $d_{x^2-y^2}$ ground state complex with oxalate in one equatorial and one axial site.

The oxalate ion. The bridging oxalato group is in each case planar within the experimental error, with Cu displaced 0.027 and 0.077 Å from the plane in the two compounds. In the Me_4en complex the oxalate occupies two equatorial sites while in the Et_5dien complex it occupies one equatorial and one axial site.

The C–C bond lengths are found within the

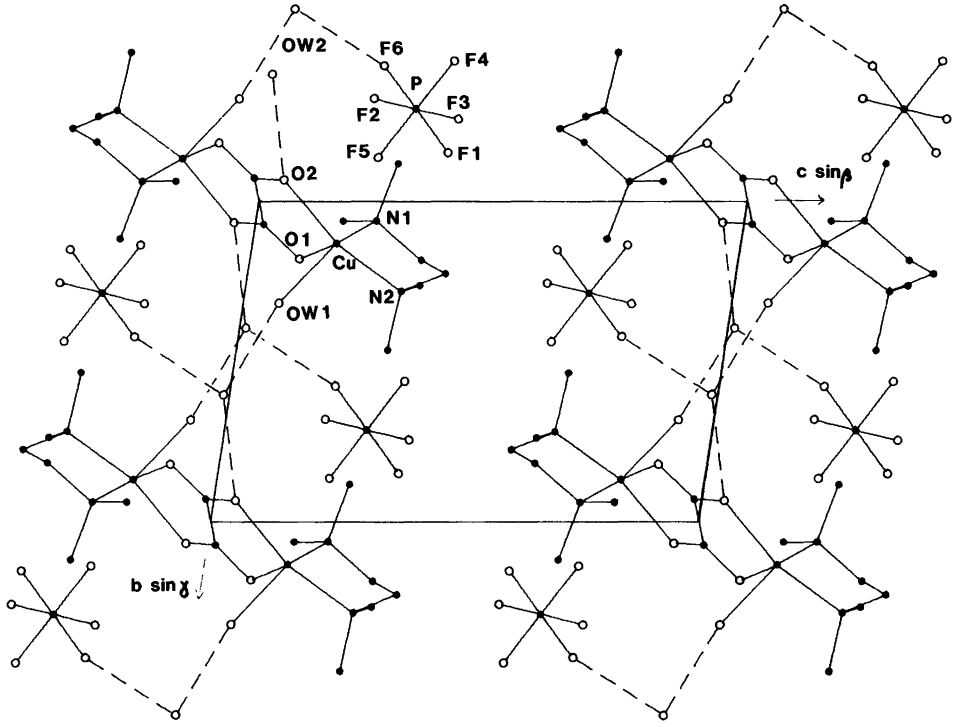

Fig. 3. Crystal packing of $[Cu_2(Me_4en)_2(C_2O_4)(H_2O)_2](PF_6)_2 \cdot 2H_2O$ as viewed down the *a*-axis. Hydrogen atoms are not drawn.

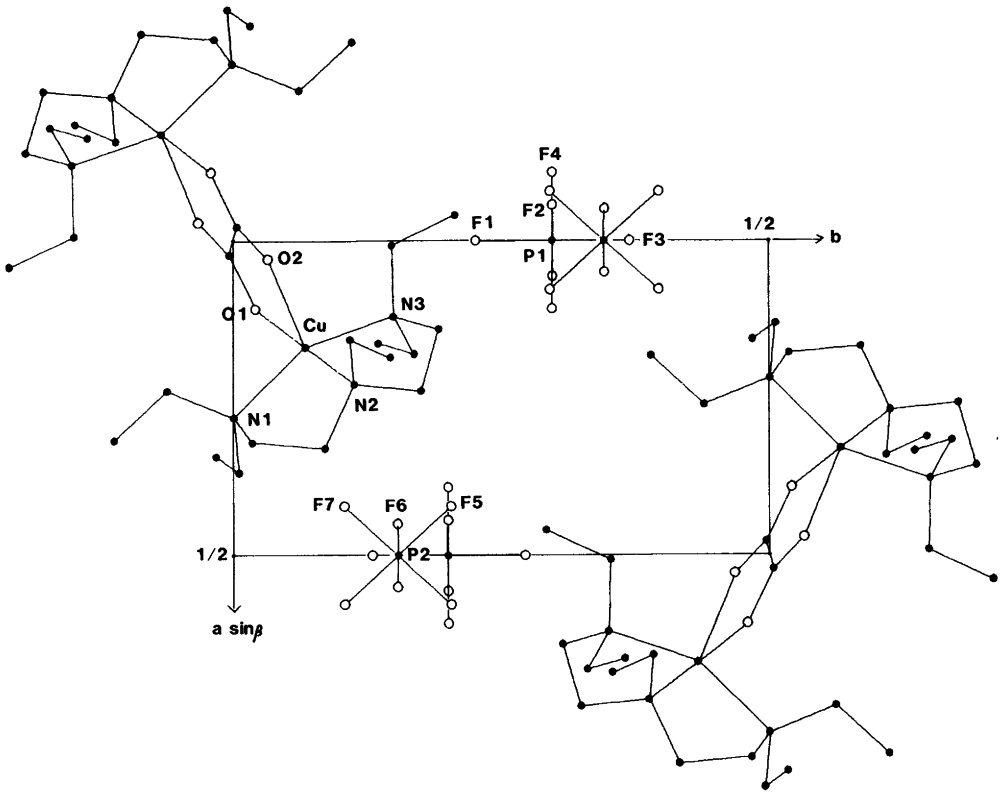

Fig. 4. Crystal packing of $[Cu_2(Et_5dien)_2(C_2O_4)](PF_6)_2$ as viewed down the *c*-axis. Hydrogen atoms are not drawn.

range normally observed for oxalic acid and oxalates (1.53–1.56 Å).[3,15,16] In the μ-oxamido complexes, on the other hand, the C–C bonds were observed to be slightly shorter than the corresponding bond in neutral oxamide.[11] In the Me_4en compound the two C–O bond lengths [1.249(9), 1.257(10) Å] are not significantly different. In the Et_5dien compound, on the other hand, there is a slight difference in C–O bond lengths [1.271(6), 1.241(7) Å] as well as in Cu–O–C angles [117.1(3), 108.9(3)°], reflecting the difference in coordination of the axial and equatorial oxygen atoms.

Phosphorhexafluoride ion. In both compounds the bond angles of the phosphorhexafluoride ions do not deviate significantly from the expected 90 and 180°. In the Me_4en compound where there is a short Cu···F5 contact as well as a hydrogen bond involving F6, the P – F bond lengths in the linear sequences F1 – P – F6 and F4 – P – F5 [1.609(6) – 1.615(6) Å] appear to be slightly different from those in the sequence F2 – P – F3 (1.585(5), 1.587(6) Å.) In the Et_5dien compound where there are no such short contacts to the fluorine atoms, the variation in P – F bond lengths of the two crystallographically independent PF_6-ions (each situated on a two-fold axis) is within the experimental error [1.587(5) – 1.603(5) Å].

Hydrogen bonding and molecular packing. In the Me_4en compound the presence of water molecules gives rise to a hydrogen bond network as depicted in Fig. 3. The coordinated water, OW1, participates in two hydrogen bonds to two water of crystallization molecules related by a centre of symmetry

$(OW1(HW11)\cdots OW2_{x+1,y+1,z}=2.842$ Å,

$OW1(HW12)\cdots OW2_{-x,-y,-z}=2.908$ Å).

The water of crystallization participates in four hydrogen bonds. In addition to the two already

mentioned, there is one hydrogen bond to F6 (OW2-(HW21)···F6=2.860 Å) and another one to O2 of the oxalate ion (OW2-(HW22)···$O2_{-x,-y-1,-z}$=2.925 Å). Only one of the hydrogen atoms on OW2 was unequivocally localized, the one pointing towards F6. However, from the remaining hydrogen bonding scheme it is clear that OW2 is a donor also in the OW2···O2 hydrogen bond. The hydrogen bonding laces the complex units together in a two dimensional network parallel to the *ab* plane, while there are no such connections parallel to *c*. This explains why the crystals easily fracture into thin platelets.

In the Et_5dien compound there is no hydrogen bonding, the structure shows discrete PF_6^- anions and dimeric cations, held together by ionic and van der Waals forces. A packing diagram is shown in Fig. 4.

Acknowledgements. Thanks are due to Professor M. Nonoyama for supplying samples of the compounds and to Professor H. Hope for placing X-ray equipment and computer facilities at my disposal during my sabbatical stay at the University of California, Davis.

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Received November 26, 1982.