Electronic Properties and Stereochemistry of the Copper(ii) Ion. Part VII.[1] Mono(diethylenetriamine)copper(ii) Complexes

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The electronic, e.s.r., and i.r. spectra of a series of polycrystalline $Cu(dien)XY.zH_2O$ and $Cu(dien)\beta X_2$ type complexes are reported, where X and Y are various anions and β = ammonia, ethylenediamine, 2,2'-bipyridyl, and diethylenetriamine. From a correlation of the three types of spectral data a tentative prediction is made of the local molecular copper(ii) ion environment present in the different complexes.

PREVIOUS papers[1] have attempted to show a relationship between the electronic properties and the stereochemistry of the local molecular environment of the copper(ii) ions present in copper(ii) complexes involving nitrogen donor ligands, such as ammonia,[2] ethylenediamine,[3] and 2,2'-bipyridyl.[1,4] The present paper describes the properties of the mono(diethylenetriamine)–copper(ii) complexes. The ligand diethylenetriamine, $C_4H_{13}N_3$ (hereafter referred to as dien) Figure IA may act as a mono-, bi-, or tri-dentate nitrogen

donor ligand. There is no X-ray crystallographic evidence that dien acts as a monodentate or bidentate ligand; it is considered to act as a bidentate ligand[5] in $Pt(dien)_2X_2$, but a number of structures are known in which it acts as a tridentate ligand to molybdenum,[6] nickel,[7] and copper[8-11] ions. When acting as a tridentate ligand, dien may assume a bent or planar configuration—Figure 1B—E; X-ray crystal structures[7-11]

[1] Part VI, B. J. Hathaway, I. M. Proctor, R. C. Slade, and A. A. G. Tomlinson, J. Chem. Soc. (A), 1969, 2219.

[2] A. A. G. Tomlinson and B. J. Hathaway, J. Chem. Soc. (A), 1968, 1905, 2578.

[3] I. M. Proctor, B. J. Hathaway, and P. Nicholls, J. Chem. Soc. (A), 1968, 1678.

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[6] F. A. Cotton and R. M. Wing, Inorg. Chem., 1965, 4, 314.

[7] P. Paoletti, S. Biagini, and M. Cannes, Chem. Comm., 1969, 513.

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[9] F. S. Stephens, J. Chem. Soc. (A), 1969, 883.

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to date indicate the latter to be the more usual con-figuration in nickel(II) and copper(II) complexes. The bent configuration has been observed in a molybdenum complex [6] Mo(dien)(CO)$_3$. There are two mono(dien)-copper(II) complexes of known structure, Figure 2, namely Cu(dien)(C$_2$O$_4$),H$_2$O [10] and [Cu(dien)(HCO)$_2$]-HCO$_2$.[11] Both complexes involve an approximately

links imposing a restricted elongated tetragonal dis-tortion on the CuN$_6$ chromophore. In Cu(dien)$_2$(NO$_3$)$_2$ both dien ligands are co-ordinated symmetrically with the central nitrogen donors co-ordinating *trans* to each other along the compressed tetragonal axis. The terminal nitrogen donors then occupy the four in-plane ligand positions.
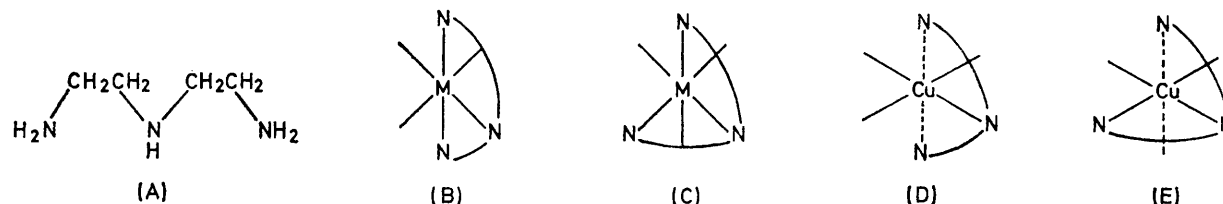

FIGURE 1   The tridentate ligand diethylenetriamine (A), when involved in a planar (B) and bent (C) conformation. In an elongated tetragonal-octahedral copper(II) ion environment both the planar (D) and bent (E) forms can impose a restricted tetragonal distortion

square-pyramidal stereochemistry with the copper(II) ion lifted significantly (by 0·2 and 0·3 Å respectively)
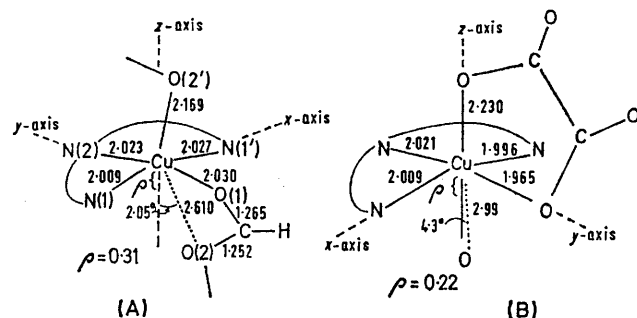

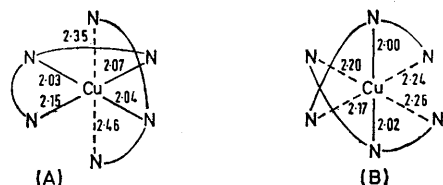FIGURE 2   The local molecular structures of (A), [Cu(dien)(HCO$_2$)]HCO$_2$ and (B), [Cu(dien)(C$_2$O$_4$)],4H$_2$O

FIGURE 3   The molecular structures of (A), Cu(dien)$_2$Br$_2$,H$_2$O and (B), Cu(dien)$_2$(NO$_3$)$_2$

out of the basal plane.   There are two bis(dien)copper(II) complexes of known crystal structure, Figure 3, namely Cu(dien)$_2$Br$_2$,H$_2$O [8] and Cu(dien)$_2$(NO$_3$)$_2$.[9] The former involves an elongated tetragonal-octahedral stereo-chemistry (Figure 3A) and the latter the much less common compressed tetragonal-octahedral stereo-chemistry (Figure 3B).   In both complexes the dien molecules assume a planar conformation.   In the bromide the two dien molecules are nonequivalently co-ordinated; one occupies three adjacent in-plane co-ordinate positions while the fourth in-plane position is occupied by the central nitrogen donor of the second dien molecule.   The two terminal nitrogen donors then occupy the axial position (above and below the in-plane CuN$_4$ chromophore) with the methylene

EXPERIMENTAL

Preparations

(A) *Mono(dien) Complexes.*—(a) Cu(dien)(NO$_3$)$_2$;   Cu-(dien)Cl$_2$. The hydrated parent copper salt (5 mmol) was dissolved in a minimum of hot methanol and to this was slowly added a hot solution of dien (5 mmol) in five times its volume of methanol. The high yield of bright blue crystals obtained, on cooling to room temperature, was removed by filtration and recrystallised from methanol.

(b) Cu(dien)Br$_2$;   Cu(dien)Cl$_2$,½H$_2$O. CuX$_2$ (5 mmol) was dissolved in a minimum of distilled water and to this was slowly added dien (5 mmol). Crystallisation was induced by addition of methanol and the blue product recrystallised from warm methanol–water (1 : 1).

(c) Cu(dien)(SO$_4$)2½H$_2$O. To CuSO$_4$,5H$_2$O (5 mmol) dissolved in a minimum of warm water was slowly added dien (5 mmol) and the resulting blue solution was allowed to evaporate slowly in a warm place. The crust of blue needle-like crystals of the 2·5 hydrate was isolated by draining off the viscous mother liquor. The mono-hydrate Cu(dien)SO$_4$,H$_2$O is readily produced by desiccation of the 2·5 hydrate under mild conditions.

(d) Cu(dien)(C$_2$O$_4$),4H$_2$O. To a suspension of Cu(C$_2$O$_4$),-½H$_2$O (5 mmol) in distilled water (10 ml) was added dien (5 mmol). The resulting aqueous solution of Cu(dien)-(C$_2$O$_4$) was filtered off and treated in the manner of method (c) to yield the tetrahydrate. Cu(dien)(C$_2$O$_4$),H$_2$O was obtained by desiccating the tetrahydrate. Cu(dien)-(PhCO$_2$),1½H$_2$O and Cu(dien)(PhCO$_2$)$_2$ were prepared similarly.

(e) Cu(dien)(NCS)$_2$. A concentrated aqueous solution of Cu(dien)SO$_4$ was prepared as in (c) to which was added an equimolar portion of solid Ba(SCN)$_2$. The mixture was stirred for 2 h after which the BaSO$_4$ was removed by filtration. Concentration of the liquor by slow evaporation gave a gum which yielded well formed crystals after redissolution in methanol and further evaporation.

(f) Cu(dien)(ClO$_4$)$_2$,H$_2$O;   Cu(dien)(BF$_4$)$_2$,H$_2$O. Evapor-ation of methanolic solutions of these complexes [prepared as in (a)] yielded only semicrystalline gums. These were redissolved in an excess of boiling isopropyl alcohol and the solution was filtered. The very finely crystallised products were obtained by setting the solutions aside in a cool place for several days.

(g) Cu(dien)(X)(ClO$_4$);   X = Cl, Br, NO$_3$, HCO$_2$, or OAc.

Equimolar portions of the two parent copper salts were added slowly to a hot solution containing two parts of dien in ten times its volume of methanol. The mixture was stirred until dissolution was complete, and was then filtered and cooled. The resulting crystalline product was recrystallised from methanol.

(h) Cu(dien)(NCS)(ClO₄); Cu(dien)(NO₂)(ClO₄). To one part of CuSO₄,5H₂O dissolved in the minimum of water was added two parts of dien. One part of Ba(NCS)₂ or

with ethanol at the point of crystallisation. Well formed crystals were obtained.

(B) Adducts of Mono(dien) Complexes.—(a) Cu(dien)-(NH₃)₂(ClO₄)₂. The parent mono(dien) complex was dissolved in the minimum of ammonia (0·880) solution. Isopropyl alcohol was added to precipitate out the poorly crystalline product.

(b) Cu(dien)(NH₃)(NO₃)₂. The parent mono(dien) complex was dissolved in the minimum of ammonia (0·880).

TABLE 1A
Analysis, e.s.r. and electronic spectra of Cu(dien)XY,zH₂O complexes

Compound	Carbon Th	Carbon F	Hydrogen Th	Hydrogen F	Copper Th	Copper F	Nitrogen Th	Nitrogen F	g_1	g_2	g_3	G	Electronic spectra (kK) § Room temp.	Low temp.	Tentative molecular structure (see Figure 4)
Cu(dien)(C₂O₄),H₂O	26·4	26·3	5·1	5·2	23·4	23·4	15·5	15·6	2·044	2·163		Ex ‡	sh, 14·5(0·8)sh	17·0sh, 14·6, 12·2sh	D
Cu(dien)(C₂O₄),4H₂O	22·4	22·4	5·4	6·4	19·5	19·4	13·2	13·1	2·043	2·167		Ex ‡	sh, 15·0(1·0)sh	17·0sh, 14·7, 12·2sh	D
Cu(dien)Br₂	14·7	14·7	4·0	4·1	19·5	19·4	13·1	13·0	2·038		2·190	5·02	sh, 15·3(1·0)	17·0sh, 15·0	C
Cu(dien)Cl₂	20·2	20·1			26·7	26·6	17·7	17·6	2·040	2·163	2·217	2·17 †	sh, 15·4(1·0)	17·2sh, 15·3	C
Cu(dien)(HCO₂)₂	28·1	28·0	5·9	5·9	24·7	24·7	16·4	16·4	2·031	2·084	2·237	4·12 †	15·6(1·7), 12·2sh	17·0sh, 15·2, 11·5sh	F
Cu(dien)(NO₃)₂	16·6	16·7	4·6	4·5	21·9	21·7	27·5	27·4	2·033	2·086	2·217	3·65 †	15·6(1·2)sh	16·3, 12·8sh	F
Cu(dien)(NCS)₂	25·5	25·3	4·6	4·7	22·5	22·5			2·055	2·181		Ex ‡	15·6(0·9)	15·6sh	C
Cu(dien)(PhCO₂)₂,1½H₂O	49·6	49·5	9·6	9·5			20·2 *	20·1 *	2·046	2·147		Ex ‡	sh, 16·0(1·2)	17·9, 15·7, 13·1	E
Cu(dien)(SO₄),H₂O	17·2	17·1	5·0	5·2	22·7	22·6	15·0	15·0	2·054		2·231	4·35	sh, 16·6(1·0)sh	sh, 16·6sh	C
Cu(dien)(SO₄),2½H₂O	15·8	15·7	6·0	6·1	20·6	20·4	13·6	13·6	2·053		2·237	4·47	sh, 16·6(1·0)sh		B or C
Cu(dien)(ClO₄)₂,H₂O	12·5	12·4	3·9	3·9	16·6	16·6			2·045		2·231	5·14	17·0(1·1)	18·6sh, 16·5	B
Cu(dien)(BF₄)₂,H₂O	13·4	13·2	4·2	4·1	17·7	17·6				2·096			17·4(1·1)	sh, 17·4, 13·3sh	B
Cu(dien)(Cl)(ClO₄)	16·0	16·1	4·5	4·4	21·5	21·5			2·053		2·172	3·25	sh, 15·6(0·9)	17·1sh, 15·2	C
Cu(dien)(HCO₂)(ClO₄)	19·3	19·3	4·5	4·4	20·4	20·2	13·1	12·9	2·048		2·183	3·81	sh, 16·0(1·3)	sh, 16·2sh	E
Cu(dien)(NCS)(ClO₄)	18·6	18·7	4·0	4·0	19·7	19·8	17·5	17·3	2·073		2·212	2·91	sh, 16·1(0·9)	18·1sh, 16·1sh	B
Cu(dien)(NO₃)(ClO₄)	14·8	14·8	4·1	4·1	19·4	19·2	17·1	17·1	2·051		2·229	4·49	sh, 16·2(1·0)	19·1sh, 16·1	E
Cu(dien)(NO₂)(ClO₄)	15·4	15·5			20·4	20·4	18·1	18·0	2·033		2·187	5·66	sh, 17·1(1·1)	19·6sh, 16·1	B
Cu(dien)Br(ClO₄)	13·9	14·0	4·0	4·0	18·8	18·8			2·061	2·252		Ex ‡	16·6(1·2)	17·4sh, 16·2	C
Cu(dien)(OAc)(ClO₄)	22·2	22·1	4·9	4·7	19·6	19·6				2·091			sh, 16·1(1·1)		
Cu(dien)Cl₂,½H₂O	19·5	19·5	5·7	5·6	25·8	25·9			2·043		2·213	4·96	sh, 16·1(1·1)	17·4sh, 15·9	B or C

* Oxygen analysis. † For three g-value spectra $g_\perp$ is taken as the mean of g_1 and g_2. § sh Indicates an unresolved shoulder; 17·0sh signifies a resolved shoulder; an indication of the relative intensity of the band maxima are given in parentheses in the arbitrary Beckman scale 0—2. ‡ The shape of the e.s.r. spectrum indicates the presence of exchange coupling.[13]

TABLE 1B
Analysis, e.s.r. and electronic spectra of Cu(dien)βX₂ complexes

Compound	Copper Th	Copper F	Hydrogen Th	Hydrogen F	Carbon Th	Carbon F	Nitrogen Th	Nitrogen F	g_1	g_2	g_3	G	Electronic spectra (kK)
Cu(dien)(NH₃)(NO₃)₂	20·6	20·5							2·048	2·075	2·184	2·80	17·7 (1·1)
Cu(dien)(NH₃)Cl₂	25·0	25·0					27·8 *	27·6 *	2·039		2·210	5·38	18·0 (1·0)
Cu(dien)(NH₃)Br₂	18·5	18·6					46·5 *	46·3 *	2·066		2·194	2·94	17·9 (1·0)
Cu(dien)(NH₃)(ClO₄)₂	16·6	16·5							2·043		2·201	4·56	18·3 (1·0)
Cu(dien)(en)Br₂	16·5	16·4					41·1 *	40·8 *	2·046		2·205	4·46	17·4 (1·1); 12·4 (0·8)
Cu(dien)(en)(ClO₄)₂	14·9	14·9	5·0	5·0	16·9	17·0			2·045		2·209	Ex.	16·6 (1·2); 11·6 (0·7)
Cu(dien)(en)(BF₄)₂	15·8	15·6	5·2	5·3	18·0	18·0	17·5	17·5	2·039		2·153	Ex.	17·0 (1·1); 12·3 (0·8)
Cu(dien)(en)(NO₃)₂	18·2	18·2	6·0	6·0	20·5	20·6			2·030		2·189	Ex.	16·1 (1·2); 12·5 (1·0)
Cu(dien)(bipy)(NO₃)₂	14·2	14·1	4·7	4·8	37·6	37·6				2·096		Isotropic	16·3 (1·0); 12·4 (0·7)
Cu(dien)(bipy)Br₂	13·1	13·1	4·4	4·5	34·8	34·8	33·1 *	32·9 *	2·047		2·198	4·21	17·4 (1·1); 13·5 (0·8)
Cu(dien)(bipy)Cl₂	16·1	16·0			42·6	42·5	18·0 *	17·8 *			2·108	Isotropic	16·1 (1·0); 12·2 (0·7)
Cu(dien)(bipy)(ClO₄)₂	12·2	12·2			32·2	32·1					2·095	Isotropic	16·4 (1·0); 12·5 (0·7)
Cu(dien)₂(NO₃)₂	16·1	16·1			24·9	24·8					2·113 †	Isotropic	16·0 (0·8); 11·4 (0·5)
Cu(dien)₂Br₂,H₂O	14·3	14·2	6·3	6·3	21·6	21·5	37·7 *	37·5 *	2·039	2·074	2·196	3·51	16·1 (0·9); 9·5 (0·6)
Cu(dien)₂Br₂	14·8	14·7	6·1	6·1	22·4	22·3				2·056	2·166	Ex.	15·9 (0·9); 11·6 (0·6)
Cu(dien)₂Cl₂	17·7	17·7	7·6	7·7	28·2	28·1	20·8 *	20·7 *	2·049		2·127	Ex.	15·9 (0·9); 10·0 (0·6)
Cu(dien)₂Cl₂,H₂O	17·7	17·6	7·2	7·1	26·8	26·6	23·4	23·3	2·057	2·072	2·193	3·00	16·1 (0·9); 9·6 (0·6)
Cu(dien)₂(OH)₂,3H₂O	17·8	17·8	7·3	7·4	26·8	26·7	23·5	23·3	2·036	2·074	2·187	3·40	16·1 (0·9); 9·5 (0·6)
Cu(dien)₂(ClO₄)₂	13·6	13·5	5·5	5·5	20·5	20·4	17·9	17·9			2·119	Isotropic	16·0 (1·0); 9·1 (0·7)
Cu(dien)₂(BF₄)₂	14·3	14·3	5·8	5·9	21·6	21·6	18·9	18·8			2·095 †	Isotropic	15·9 (0·9); 1·15 (0·6)

* Halogen Analysis. † Recorded at liquid-nitrogen temperature.

Ba(NO₂)₂ was added and the mixture was stirred until all the barium salt had dissolved. The BaSO₄ was removed by filtration to give concentrated aqueous solutions of Cu(dien)₂(NCS)₂ or Cu(dien)₂(NO₂)₂ to which one part of Cu(ClO₄)₂,6H₂O was added, dissolved in the minimum of water. The crude product was precipitated by slow addition of ethanol and then recrystallised from warm methanol.

(i) Cu(dien)(HCO₂)₂. Cu(HCO₂)₂,4H₂O (5 mmol) was added to a solution of dien (5 mmol) in hot methanol. The filtered hot solution was cooled and carefully covered

The solution was placed in a closed container and cooled to 0 °C for one day. Crystals were formed.

(c) Cu(dien)(NH₃)Cl₂. Ammonia gas was passed through a concentrated methanolic solution of Cu(dien)Cl₂; the liquid evaporated slowly to leave a gum. Crystals were produced on trituration in the presence of isopropyl alcohol.

(d) Cu(dien)(NH₃)Br₂. A cooled solution prepared as in (b) was triturated in the presence of isopropyl alcohol and covered with ether to precipitate the very soluble product.

(e) Cu(dien)(en)X$_2$ (X = Br$^-$, NO$_3$$^-$, BF$_4$$^-$, or ClO$_4$$^-$). One part each of ethylenediamine and diethylenetriamine were added slowly to a hot methanolic solution of the parent copper salt such that no solid product was directly formed. On cooling, the hot solution yielded crystals which were recrystallised from methanol–ethanol (1 : 1).

(f) Cu(dien)(bipy)(ClO$_4$)$_2$. Cu(ClO$_4$)$_2$,6H$_2$O (3 mmol) was dissolved in the minimum of warm methanol to which were added dropwise solutions of dien (3 mmol) and bipy (3 mmol) in ten times their bulk of methanol. The sparingly

(c) Cu(dien)$_2$Br$_2$,H$_2$O. The crude product, obtained by method (C) (a), was added to a cool mixture of iso-propyl alcohol–water (4 : 1); the solution was filtered and set aside for several days.

(d) Cu(dien)$_2$(OH)$_2$,3H$_2$O. This compound was the product obtained by setting aside over NaOH for 3 weeks the gum obtained by evaporation of aqueous Cu(dien)$_2$(NO$_3$)$_2$ solution; this preparation could not be repeated. Other preparative methods failed to yield stable or crystalline products.

TABLE 2A

Infrared spectra of polyanions present in Cu(dien)XY,zH$_2$O complexes

Compound	Infrared bands and assignment	v_1/v_3 (%) *	Inference
Cu(dien)(NO$_3$)(ClO$_4$)	1505s,b; ~1290m,b(v_3 split); 961m(v_1); 810m,sp(v_2); 748(v_4 split)		Co-ordinated nitrate
	~1100s,b(v_3); 935w(v_1); 613s,sp(v_4); 469w(v_2)	15	Semi-co-ordinated perchlorate
Cu(dien)(NO$_3$)$_2$	1485s; 1280b(v_3 split); 982s(v_1); 814m,sp(v_2); 740w,sp; ?(v_4 split)		Co-ordinated nitrate
	~1365b(v_3); 835w,sp(v_2)		Ionic nitrate
Cu(dien)(ClO$_4$)$_2$,H$_2$O	~1070s,vb(v_3); 931sh(v_1); 622s,sp(v_4); 475w(v_2) 825m,b(M–OH$_2$)	20	Semi-co-ordinated perchlorate Co-ordinated water
Cu(dien)(NCS)$_2$	2100s,sp[v_1(CN)]; 802w[v_3(CS)] 2075s,sp[v_1(CN)]; 768w[v_3(CS)]; 467 [v_2(NCS)]		Co-ordinated thiocyanate Ionic thiocyanate
Cu(dien)(BF$_4$)$_2$,H$_2$O	~1020s,b(v_3); 768w,sp(v_1) 725s,b	20	Semi-co-ordinated borofluoride Co-ordinated water
Cu(dien)Cl(ClO$_4$)	1075s,b(v_3); 932w(v_1); 621s,sp(v_4); 463w(v_2)	20	Semi-co-ordinated perchlorate
Cu(dien)(NCS)(ClO$_4$)	~1080s,b(v_3); v_1 absent; 621s,sp(v_4) 2120s,sp[v_1(CN)]; 805w[v_3(CS)]	0	Ionic perchlorate Co-ordinated thiocyanate
Cu(dien)Br(ClO$_4$)	~1080s,b(v_3); 943w,sp(v_1); 621s,sp(v_4); 465w,sh(v_2)	30	Semi-co-ordinated perchlorate
Cu(dien)(NO$_2$)(ClO$_4$)	~1090s,b(v_3); 938vw(v_1); 622s,sp(v_4); 464vw(v_2) ~1320m,b(v_1); 837(v_3)(δONO)	5	Ionic perchlorate Co-ordinated nitro
Cu(dien)(SO$_4$),2½H$_2$O	1165s,b, 1105s,br, 1045s,b(v_3 split); 955s(v_1); 580—610; 638(v_4 split); 460s(v_2)		Bidentate (?) Co-ordinated sulphate
Cu(dien)(SO$_4$),H$_2$O	1165s,b, 1105sb, 1045s,b(v_3 split); 952(v_1); 580—610, 635(v_4 split); 463s(v_2)		Bidentate (?) Co-ordinated sulphate
Cu(dien)(C$_2$O$_4$),H$_2$O	1667(v_{as}); 1428(v_3)		Co-ordinated oxalate
Cu(dien)(C$_2$O$_4$),4H$_2$O	1650s(H$_2$O + v_{as}); 1424(v_3)		Co-ordinated oxalate
Cu(dien)(OAc)(ClO$_4$)	1405(v_s — CO$_2$); 1560(v_{as} — CO$_2$) 1100s(v_3); 920w(v_1)	15	Ionic or bidentate acetate Semi-co-ordinated perchlorate
Cu(dien)(HCO$_2$)(ClO$_4$)	1572(v_{as} — CO$_2$); 1344(v_3 — CO$_2$) 795(v — CO$_2$) 1105(v_3); 923w(v_1)	15	Ionic or bidentate formate Semi-co-ordinated perchlorate
Cu(dien)(HCO$_2$)(HCO$_2$)	1575—1525(v_{as} — CO$_2$); 1380—1300(v_3 — CO$_2$) 800s, 753s(vCO$_2$)		Two types of formation

* v_1/v_3 (%) Refers to the ratio of the peak heights of the v_1 and v_3 bands expressed as a percentage.

soluble complex precipitated immediately and was re-crystallised from a large volume of methanol with a little water added to increase solubility.

(g) Cu(dien)(bipy)X$_2$; X = NO$_3$, Cl, or Br. To a hot methanolic solution of the parent copper salt prepared by dissolving the salt (3 mmol) in the minimum of methanol were added hot solutions of dien (3 mmol) and bipy (3 mmol) in ten times their bulk of methanol. Crystals formed on cooling.

(C) Bis(diethylenetriamine) Complexes.—(a) Cu(dien)$_2$-(NO$_3$)$_2$; Cu(dien)$_2$Cl$_2$,H$_2$O; Cu(dien)$_2$Br$_2$. A stoicheio-metric portion of the ligand was added to a hot concentrated methanolic solution of the appropriate copper salt; the solution was filtered and quickly cooled. The resultant crude product was recrystallised from hot methanol.

(b) Cu(dien)$_2$(ClO$_4$)$_2$; Cu(dien)$_2$(BF$_4$)$_2$; Cu(dien)$_2$Cl$_2$. A hot concentrated methanolic solution of the crude product obtained by method (C) (a), was added to a large volume of warm isopropyl alcohol and quickly cooled.

Microanalysis was carried out by A. Bernhardt, 433 Mulheim (Ruhr) Germany, for carbon, hydrogen, nitrogen and in one case oxygen, by difference. The copper and halogen were estimated gravimetrically as the Cu(en)$_2$HgI$_4$ and AgX salts, respectively, after initial oxidation of the weighed quantity of complex by digestion for 2—3 h with

TABLE 2B

The i.r. spectra of polyatomic anions present in Cu(dien)βX$_2$ complexes

Complex	v_3	v_1	v_2
Cu(dien)(NH$_3$)(NO$_3$)$_2$	1350s,vb		832m
Cu(dien)(en)$_2$(NO$_3$)$_4$	1350s,b		830m
Cu(dien)(bipy)(NO$_3$)$_2$	1330s,b		833m
Cu(dien)$_2$(NO$_3$)$_2$	1350s,b		833m
Cu(dien)(NH$_3$)(ClO$_4$)$_2$	1090vs,b	933w	615vs
Cu(dien)(en)(ClO$_4$)$_2$	1095vs		
Cu(dien)(bipy)(ClO$_4$)$_2$	1090vs	937vw	
Cu(dien)$_2$(ClO$_4$)$_2$	1085vs		617s
	v_3	v_1	v_4
Cu(dien)(en)(BF$_4$)$_2$	1045s,b	772vw	
Cu(dien)$_2$(BF$_4$)$_2$	1075s,b	772w	521s

potassium persulphate. The analyses are given in Tables 1A and 1B.

Physical Measurements.—These measurements were determined using polycrystalline samples as reported previously;[1] the results are given in Tables 1A, 1B, 2A and 2B.

DISCUSSION

E.s.r. Spectra.—The observed g-values, obtained from the spectra of polycrystalline samples,[12] are listed in Tables 1A and 1B. The g-values all lie in the range 2·0—2·30 with no absorption at high or low fields; the spectra are consistent with magnetically dilute copper(II) ion environments[13] and with the absence of any strong copper–copper interaction, as in [Cu-(CH$_3$CO$_2$)$_2$H$_2$O]$_2$. The complexes of Table 1 may therefore be considered with respect to their electronic properties as mononuclear species, with the empirical formula as listed. If any of the anions present are bridging anions between separate copper(II) ions, this cannot involve any significant spin–spin interaction. Such interaction might be expected to occur in {Cu-(dien)(HCO$_2$)}HCO$_2$, whose structure involves a bridging formato-group, with short copper–oxygen bond lengths 2·030 and 2·169 Å. However, a room-temperature magnetic moment[14] of 1·95 B.M. and a Weiss constant of $-5°$ gives no indication of significant magnetic interaction down to liquid-nitrogen temperatures.

The polycrystalline e.s.r. spectra of Tables 1A and 1B exhibit isotropic, exchange coupled (see Figure 7F, ref. 12), two g-value or three g-value spectra. The first two types arise in the present complexes from exchange coupling[12] through misalignment of the local molecular axes between the different molecules in the unit cell ($Z > 1$). These types of spectra unfortunately give no information on the electronic ground state of the copper(II) present. This is particularly unfortunate in the case of Cu(dien)$_2$(NO$_3$)$_2$ which is known to have a compressed tetragonal-octahedral stereochemistry[9] which gives rise to a d_{z^2} ground state. In this complex the four molecules in the unit cell are so misaligned that exchange coupling results in the observation of an isotropic e.s.r. spectrum.[15] Exchange coupling is not ruled out for the two and three g-value spectra, but is small if G lies between 3·0 and 5·0, where $G = (g_3 - 2)/(g_\perp - 2)$ for two g-value spectra, and $G = (g_3 - 2)/(g_\perp - 2)$ for three g-value spectra {where $g_\perp = (g_1 + g_2)/2$}. For complexes with G within this range, the observed lowest g-value [$g_\perp$ for the two g-value spectra and $(g_1 + g_2)/2$ for three g-value spectra] all

lie above 2·04 consistent[3,4,12] with a $d_{x^2-y^2}$ (or less probably[12] a d_{xy}) ground state for the copper(II) ion environment. None of the complexes have a sufficiently small, lowest g-value to suggest a d_{z^2} ground state and hence[12] a compressed-tetragonal or rhombic-octahedral, trigonal-bipyramidal or *cis*-distorted octahedral environment for the copper(II) ion is ruled out.

I.r. Spectra.—The i.r. spectra of the diethylenetriamine ligands in the Cu(dien)XY,2H$_2$O and Cu(dien)-βX$_2$ type complexes are very similar[16] to that of the free ligand and are not reported in detail (but see ref. 16). Although it has been suggested[17,18] in the literature that the planar and facial conformations of the dien ligand may be distinguished by their i.r. spectra it was not found possible to establish an i.r. criterion for the planar conformation even when this was known to be present from the X-ray crystal structure[8-11] (Figures 2 and 3).

The i.r. spectra of the polyanions present in the Cu(dien)XYzH$_2$O complexes are given in Table 2. I.r. criteria[19] for the mode of bonding of a symmetrical polyatomic anion to a transition-metal ion are now established, and it is possible to distinguish ionic and co-ordinated polyatomic anions. In the particular instance of copper(II) complexes it is also necessary to consider the structural situation referred to as semi-co-ordination,[3] particularly for the anions perchlorate, tetrafluoroborate, and sulphate, for which an i.r. criterion[12,20] for s emi-co-ordination has also been established. A further structural situation can also occur in axial copper(II), when co-ordinated by anions such as, nitrite, nitrate,[22] formate,[11] or monochloroacetate.[23] The anions may co-ordinate through an oxygen atom in the equatorial plane (Cu–O, *ca.* 2·0 Å) but may also involve co-ordination of a terminal oxygen atom at *ca.* 2·3—2·9 Å out of the equatorial plane and off the z-axis. In this structural situation this long copper–oxygen ' bond ' makes an angle of 30—40° to the z-axis, a feature imposed by the ligand geometry of the anion and the non-spherical character of the copper(II) ion. The effect[24] of this off-z-axis co-ordination on the electronic properties of the copper(II) ion is small and consequently its effect on the i.r. spectra of the co-ordinated polyatomic anion is also small, for this reason it is not possible to establish an i.r. criterion of off-z-axis co-ordination by these polyatomic anions. Thus, although the i.r. data of Table 2 may be used as evidence of primary co-ordination it does not yield evidence of off-the-z-axis co-ordination by these anions.

[12] B. J. Hathaway and D. E. Billing, *Co-ordination Chem. Rev.*, 1970, **5**, 143.

[13] J. Lewis, F. E. Mabbs, L. K. Royston, and W. R. Smail, *J. Chem. Soc. (A)*, 1969, 291; J. H. Price, J. R. Pilbrow, K. S. Smith, and T. D. Smith, *J. Chem. Soc. (A)*, 1970, 968.

[14] M. J. Bew, R. J. Dudley, R. J. Fereday, B. J. Hathaway, and R. C. Slade, *J. Chem. Soc. (A)*, 1971, 1437.

[15] B. J. Hathaway, M. J. Bew, and D. E. Billing, *J. Chem. Soc. (A)*, 1970, 1090.

[16] M. J. Bew, Ph.D. Thesis, University of Essex, 1970.

[17] D. A. House and C. S. Garner, *Inorg. Nuclear Chem. Letters*, 1965, **1**, 137; D. A. House and C. S. Garner, *Nature*, 1965, 208, 776; D. A. House, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 67.

[18] H. H. Schmidtke and D. Gartoff, *Inorg. Chim. Acta*, 1968, **2**, 357.

[19] K. Nakamoto, ' Infrared Spectra of Inorganic and Co-ordination Compounds,' John Wiley, New York, 1963.

[20] B. J. Hathaway and A. A. G. Tomlinson, *Co-ordination Chem. Rev.*, 1970, **5**, 1.

[21] F. S. Stephens, *J. Chem. Soc. (A)*, 1969, 2082.

[22] A. F. Cameron, D. W. Taylor, and R. H. Nuttall, *Chem. Comm.*, 1971, 253.

[23] G. Davy and F. S. Stephens, *J. Chem. Soc. (A)*, 1971, 1917.

[24] D. E. Billing, B. J. Hathaway, and P. Nicholls, *J. Chem. Soc. (A)*, 1970, 1877; R. J. Dudley, B. J. Hathaway, and P. G. Hodgson, *ibid.*, 1971, 3358.

In general the i.r. data for Cu(dien)XY,zH$_2$O complexes is consistent with the presence of one co-ordinated anion X and one semi-co-ordinate or ionic anion; this was the situation in [Cu(dien)(HCO$_2$)]HCO$_2$, a result which has since [11] been established by X-ray crystallography. Less convincing is the evidence for semi-co-ordination of the perchlorate or tetrafluoroborate ions; this is indicated [3] by a broadening of ν_3 at 1100 cm^{-1} (rather than the complete splitting shown on true co-ordination) and an increase in the relative intensity of the ν_1 mode to 30—40% of that of ν_3. ν_1 Is forbidden in the free ion, but fully allowed in the covalently bonded perchlorate group.[25] In the Cu(dien)XY,zH$_2$O complexes the ratio of ν_1/ν_3 does not rise above 30%, it is highest when X = chloride or bromide ion and in [Cu(dien)(H$_2$O)](BF$_4$)$_2$ and [Cu(dien)(H$_2$O)](ClO$_4$)$_2$; and lowest when X = nitro and thiocyanate anions. Since the dien ligand can only be involved in σ-bonding, this difference may be associated with the differing π-bonding potential [26] of the ligands X. For X = Cl$^-$, Br$^-$, and H$_2$O little or no π-bonding occurs and the additional bonding requirement of the coplanar CuN$_3$X chromophore is supplied by semi-co-ordination of a perchlorate or tetrafluoroborate anion above and below the equatorial plane resulting in i.r. evidence of semi-co-ordination of these anions. When X = NO$_2$$^-$ or NCS$^-$, extensive π-bonding can occur, which satisfies the additional bonding requirement of the coplanar CuN$_3$X chromophore, consequently the perchlorate anions in these complexes are not involved in semi-co-ordination to the copper(II) ion and their i.r. spectra indicate ionic anions. The i.r. spectra of the two sulphate complexes both indicate co-ordinated [19] sulphate groups. As both complexes also contain water, it is not possible to distinguish between a molecular structure involving in-plane co-ordination of the sulphate group and one involving a bridging semi-co-ordinate sulphate group with a molecule of water occupying the fourth in-plane co-ordinate position on the copper(II) ion. A comparable structure exists [27] in Cu(en)(H$_2$O)SO$_4$ and for this reason the latter possibility is preferred.

The i.r. spectra associated with the polyatomic anions present in the complexes of Table IB are shown in Table 2B. They are all consistent with the presence [19] of ionic anions and give no evidence of covalent bonding to the copper(II) ions and support the earlier suggestion that the nitrogen ligands present are preferentially co-ordinated to the copper(II) ions. What is surprising is that there is no i.r. evidence for semi-co-ordinated [3] perchlorate ions in Cu(dien)(NH$_3$)(ClO$_4$)$_2$, in which the presumably planar CuN$_3$N$_1$' chromophore involving four σ-bonding nitrogen ligands would be expected to involve the perchlorate anions in semi-co-ordination in order to satisfy the additional out-of-plane bonding [12]

required by such a chromophore. While the perchlorate i.r. band, ν_3 is very strong and broad, the intensity of ν_1 is only weak ($\nu_1/\nu_3 = 5\%$) (for semi-co-ordination $\nu_1/\nu_3 = 30$—40%). Why there is no evidence for semi-co-ordination in Cu(dien)(NH$_3$)(ClO$_4$)$_2$ is not understood. If the complexes containing the CuN$_3$N$_2$' chromophore involve a square-pyramidal stereochemistry (see later) it is not surprising that the polyanions are ionic as in this stereochemistry [12] even if they occupy the sixth co-ordination position this is usually at such a distance ca. 3·0 Å, that even semi-co-ordination would be weak. In complexes containing the CuN$_6$ chromophore the polyanions would be expected to be ionic as they are unable to compete with the nitrogen donor ligands present.

Electronic Spectra.—The Cu(dien)XY,zH$_2$O complexes are all blue; their electronic reflectance spectra, with
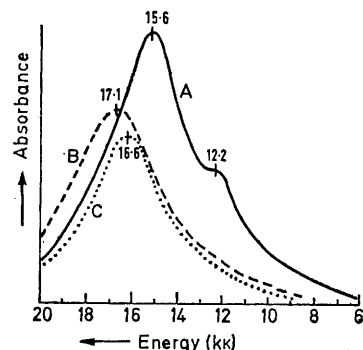
FIGURE 4 The electronic reflectance spectra of Cu(dien)XY,zH$_2$O complexes: A, [Cu(dien)(HCO$_2$)]HCO$_2$; B, Cu(dien)(NO$_2$)(ClO$_4$); C, Cu(dien)(H$_2$O)(SO$_4$),1·5H$_2$O

one exception, are all comparable, consisting of a broad maximum in the range 14·5—17·4 kK with evidence of a shoulder to high or low energy. These shoulders are not usually resolved at room temperature (Table IA and Figure 4) but better resolution is generally obtained at the temperature of liquid nitrogen, with the band maxima shifted ca. 0·5 kK to higher energy. The exception [14] is the spectrum of [Cu(dien)(HCO$_2$)]HCO$_2$, with a significantly more intense band maximum at 15·6 kK and a clearly resolved shoulder at 12·2 kK.

Taken together the e.s.r., i.r., and electronic spectra of the Cu(dien)XY,zH$_2$O complexes suggest an elongated axial environment for the local copper(II) ion environment, most probably involving a rhombic octahedral or square-pyramidal stereochemistry. These possibilities are depicted in Figure 5B—E taking into account the structural properties of the anions present. They reflect varying extents of tetragonal distortion which is greatest in the square-coplanar stereochemistry and least in the square-pyramidal stereochemistry with a short copper to fifth ligand bond-length. The latter extreme (Figure 5F) is illustrated by [Cu(dien)(HCO$_2$)]HCO$_2$ [11] in which not only is there an extremely short copper-fifth ligand bond-length of 2·169 Å, but

[25] B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 1961, 3091.

[26] H. B. Gray, 'Electrons and Chemical Bonding,' W. A. Benjamin, New York, 1965, p. 198.

[27] M. Dunai-Junio and M. A. Porai-Koshits, *Chem. Zvesti*, 1961, **20**, 783.

the sixth co-ordination position also involves a potential ligand in the terminal formate oxygen atom in an off-the-z-axis position at 2·610 Å. This structure results in the lowest-energy electronic spectrum of any complex and as the structure clearly lacks a centre of symmetry, the most intense spectrum of the series. The Cu(dien)-$(C_2O_4),4H_2O$, while still five-co-ordinate (Figure 2B and

(A) Square coplanar

(B) Rhombic octahedral

(C) Square pyramidal

(D) Square pyramidal (chelate)

(E) Square pyramidal (off-axis-ligand)
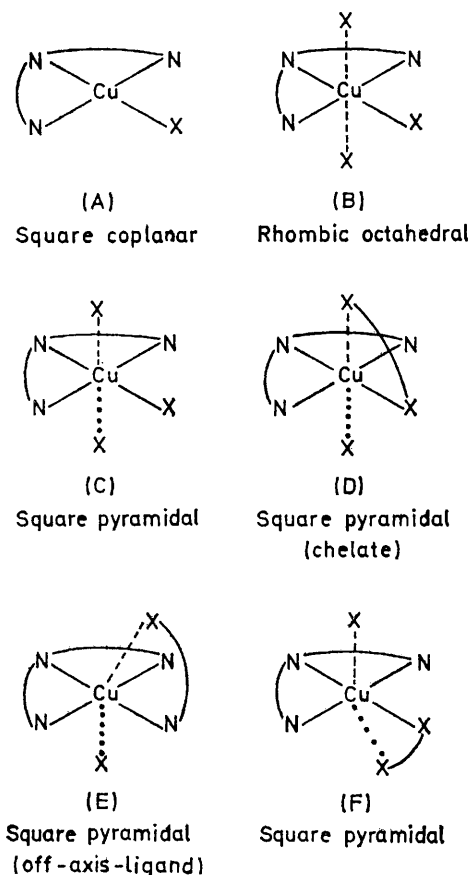
(F) Square pyramidal

FIGURE 5 Suggested possible stereochemistries for Cu(dien)XY,zH$_2$O complexes

5D), involves a longer copper-fifth ligand bond-length and hence the electronic spectrum lies to slightly higher energy, the low-frequency shoulder is not resolved and the whole spectrum is less intense than the formate. Complexes with a band maximum in the higher energy region 16—17·0 kK equate with a higher tetragonal distortion. The square-coplanar stereochemistry (Figure 5A) has been considered unlikely [12,28] with three in-plane σ-bonding nitrogens, unless L is a potentially π-bonding ligand, such as nitro- or thiocyanato-groups. These complexes do have band maxima at the higher energy end of the observed range, namely 16—17 kK. If L is a pure σ-bonding ligand as in water, then the additional bonding potential of the CuN$_3$O chromophore is supplied by semi-co-ordinating perchlorate groups (see i.r. section) and the rhombic octahedral stereochemistry Figure 5B is appropriate with a high tetragonal distortion and hence relatively high band maximum in the electronic spectra. Thus [Cu(dien)(H$_2$O)](ClO$_4$)$_2$

has a band maximum at 17·0 kK with no indication of a high- or low-energy shoulder, a comparable spectrum [3] to the tetragonal-octahedral Cu(en)$_2$(ClO$_4$)$_2$ complexes with a single maximum at 18·8 kK. Those remaining complexes with a band maximum in the region of 15·0 kK probably involve essentially coplanar CuN$_3$L chromophores with a rather long-bonded fifth ligand co-ordinating either along the z-axis (Figure 5C) or off-the-z-axis with the appropriate anion ligand X (Figure 5E). Thus [Cu(dien)Cl]ClO$_4$ probably involves an in-plane Cu–Cl bond of 2·30 Å with a long Cu–Cl bond of 2·7 Å by bridging between the separate CuN$_3$Cl chromophores, plus a semi-co-ordinated perchlorate ion at 2·65 Å. The slightly short copper–chlorine bond out-of-the-plane then reduces the tetragonal distortion present and hence the energy of the band maximum to 15·6 kK. [Cu(dien)-(NO$_3$)]ClO$_4$ and [Cu(dien)(OAc)]ClO$_4$ have virtually identical electronic spectra, 16·2 and 16·1 kK respectively. Both involve co-ordinated polyanions in the CuN$_3$O plane, but in order to reduce the energy of the band maxima to ca. 16·2 kK, they require the additional involvement of a terminal oxygen atom in off-axis co-ordination. In both cases the perchlorate ions are involved in weak semi-co-ordination ($\nu_1/\nu_3 = 15\%$) in the sixth co-ordinate position. The electronic spectra of the Cu(dien)SO$_4$,zH$_2$O complexes suggest similar molecular environments for the copper(II) ion. The i.r. spectra suggest a bidentate sulphate ion presumably bridging to a further copper(II) ion to form a rhombic-octahedral or square-pyramidal stereochemistry (see i.r. section). The electronic spectra do not allow a distinction to be made between these two possibilities. The electronic spectrum of Cu(dien)(NO$_3$)$_2$ is unique; it clearly differs from that of [Cu(dien)(NO$_3$)]ClO$_4$ in that the band maximum is at lower energy and there is an unresolved low-frequency shoulder. If there is any resemblance to another spectrum it is to that of [Cu-dien)(HCO$_2$)]HCO$_2$ except that the intensity is not quite as high (1·2 compared with 1·7). This would suggest a comparable molecular structure to the formate, namely Figure 5F but with a slightly higher tetragonal distortion.

These tentative conclusions concerning the stereochemistry of the Cu(dien)XY,zH$_2$O complexes are summarised in the last column of Table 1A using the letters of Figure 5. The Cu(dien)βX$_2$ complexes are all blue/purple and their electronic reflectance spectra may be divided into two classes: viz. those having a single broad band at 17·7—18·3 kK and a less intense shoulder or clearly resolved band at 9·1—13·5 kK (Figure 6). The first class of spectra are restricted to the Cu(dien)(NH$_3$)X$_2$ complexes involving the CuN$_4$ chromophore. The close similarity in energy of the spectra of the four complexes of this type, 17·7—18·3 kK suggest that all four have the same environment for the copper(II) ion. One complex, the perchlorate, yielded definitive e.s.r. data, consistent with a $d_{x^2-y^2}$ (or d_{xy})

[28] B. J. Hathaway and F. S. Stephens, *J. Chem. Soc. (A)*, 1970, 884.

ground state. Both the e.s.r. and electronic spectra are consistent [29] with a square-coplanar stereochemistry but do not rule out an elongated tetragonal-octahedral
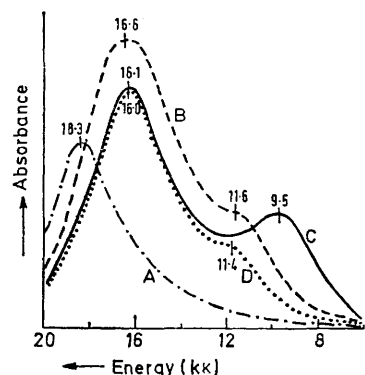

FIGURE 6 The electronic reflectance spectra of $Cu(dien)\beta X_2$ complexes: A, $Cu(dien)(NH_3)(ClO_4)_2$; B, $Cu(dien)(en)(ClO_4)_2$; C, $Cu(dien)_2Br_2,H_2O$ and D, $Cu(dien)_2(NO_3)_2$

(A)
Rhombic octahedral

(B)
Square pyramidal

(C)
Rhombic octahedral

(D)
Tetrahedral twisted

(E)
Square pyramidal

(F)
Rhombic octahedral
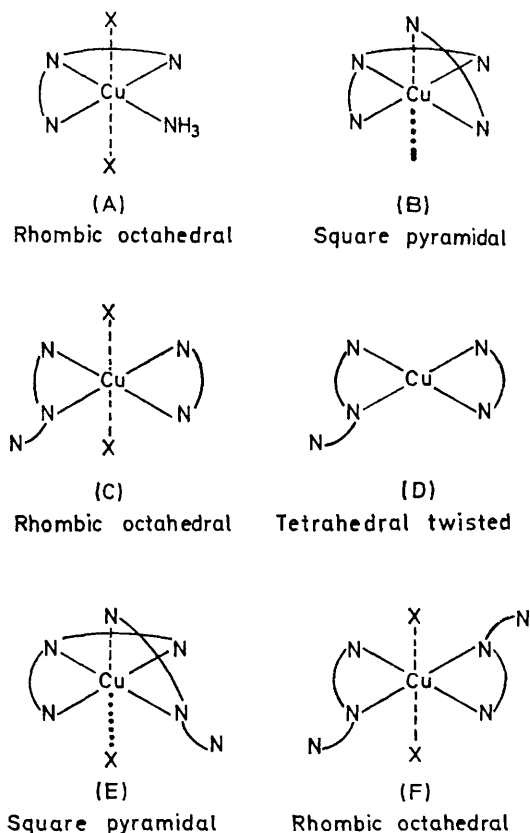
FIGURE 7 Suggested possible stereochemistries for $Cu(dien)\beta X_2$ complexes

one especially as there is no X-ray crystallographic evidence for a strictly square-coplanar CuN_4 stereochemistry involving σ-bonding nitrogen ligands.[28] The observed values for the $Cu(dien)(NH_3)X_2$ complexes of 17·7—18·3 kK would therefore suggest that these

[29] B. J. Hathaway, *J.C.S. Dalton*, 1972, 1196.
[30] J. E. Johnson, T. A. Beineke, and R. A. Jacobson, *Acta Cryst.*, 1969, **A25**, S164.

complexes also have an elongated rhombic octahedral stereochemistry (Figure 7A) in spite of the lack of i.r. evidence for semi-co-ordinated perchlorate ion in one of them.

The electronic spectra of the remaining complexes although very similar, may be further sub-divided depending on the number of potential nitrogen donor ligands, namely CuN_5 and CuN_6 present. The spectra of these two classes will therefore be discussed separately.

The electronic spectra of the CuN_5 chromophore-containing complexes are very similar. The maxima vary in energy from 16·1—17·4 kK and the shoulder from 11·6—13·5 kK with the low-frequency shoulder 30% less intense than the band maximum and not always clearly resolved. Only two of the eight complexes in this class yielded definitive e.s.r. data, but the two that did, clearly suggest a $d_{x^2-y^2}$ or d_{xy} ground state. Reference to Figure of ref. 29 suggests that the most obvious stereochemistry for these eight complexes is square pyramidal (Figure 7B), with or without one of the anions present occupying the sixth co-ordination position but at a long distance (*ca.* 3·0 Å). A rhombic octahedral stereochemistry is possible if the dien only acts as a bidentate ligand, with the two anions occupying the fifth and sixth axial positions (Figure 7C). This structure is rather unlikely as it implies a preferential co-ordination of the copper(II) ions by anions rather than by a nitrogen donor (there is no i.r. evidence [3] for semi-co-ordinated polyanions) and it is difficult to rationalise the low energy of the shoulder in the electronic spectra with this stereochemistry.[12,29] A distorted tetrahedral stereochemistry is possible (Figure 7D), if the dien acts only as a bidentate ligand. Such a stereochemistry would explain the failure to observe any i.r. evidence for semi-co-ordinated perchlorate ions and is consistent with the presence of a low-frequency shoulder. The structure would then be comparable with that of $Cu(bipyam)_2(ClO_4)_2$ [30] which has a distorted CuN_4 chromophore (dihedral angle = 56°). The perchlorate groups are not involved in semi-co-ordination ($Cu-O = ca.$ 4·0 Å) and the electronic spectrum [31] has a strong band at 18·4 kK, a clear shoulder at 10·4 kK, and evidence of a weak shoulder at 13·5 kK. Notwithstanding this comparison, it is difficult to understand why the dien should only function as a bidentate ligand and restrict the co-ordination number of the copper(II) ion to four; especially as all four copper(II)–dien complexes of known crystal structure involve the ligand functioning as a tridentate chelate. Attempts [16] to effect this by preparing complexes involving the partially protonated dien, namely dien H^+ and dien H_2^{2+} as a ligand, failed although a copper complex [32] involving the fully protonated dien H_3^{3+} cation is known, (dien $H_3)(CuCl_4)Cl$.

The electronic spectra of the CuN_6 chromophore-

[31] W. R. McWhinnie, *J. Chem. Soc. (A)*, 1964, 5165; R. J. Dudley, B. J. Hathaway, and P. G. Hodgson, *J.C.S. Dalton*, 1972, 882.
[32] B. Zazlow and G. A. Ferguson, *Chem. Comm.*, 1967, 822.

containing complexes consist of a band maximum at 15·9—16·1 kK and a low-frequency shoulder of half the intensity of the band maximum in the range 9·1—11·6 kK. The complexes may be further sub-divided according to the energy of the low-frequency shoulder: the lower the energy (9·1—10·0 kK) the more clearly is this band resolved, while at higher energy (11·4—11·6 kK) the band only appears as a shoulder (Figure 6). Of the eight complexes in this class three have a high-energy shoulder and five a low-energy shoulder. Of the latter, three of the complexes give rise to three g-value e.s.r. spectra which are consistent with a $d_{x^2-y^2}$ ground state. This suggests that all the complexes having this type of electronic spectrum have the elongated tetragonal-octahedral stereochemistry known [8] to be present in $Cu(dien)_2Br_2H_2O$, Figure 3A, involving a restricted tetragonal distortion, imposed by the out-of-plane chelation of one of the dien ligands, which is responsible for the low-energy of the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition.[33]

All three of the complexes involving a higher-energy shoulder (11·4—11·6 kK) yield isotropic or exchange coupled e.s.r. spectra and therefore do not yield a clear indication of the electronic ground state. This is very unfortunate as one of these complexes $Cu(dien)_2(NO_3)_2$ has the very uncommon compressed tetragonal octahedral stereochemistry (Figure 3B) and a definitive indication of the ground state for this stereochemistry would be invaluable.[15] In the absence of definite e.s.r. data and in view of the similiarity of their electronic spectra, it is tentatively suggested that all three complexes have the compressed tetragonal octahedral stereochemistry. The possibility of a CuN_5 or CuN_4 chromophore being present in these complexes with one (or two) (Figure 7E and F) of the dien ligands present acting as bidentate ligands cannot be ruled out, especially in view of the two entirely different modes of bonding of the two dien ligands in $Cu(dien)_2$-BrH_2O.[8] But as both of the $Cu(dien)_2X_2$ complexes of known crystal structure involve a CuN_6 chromophore, this possibility seems unlikely.

[33] B. J. Hathaway, M. J. Bew, D. E. Billing, R. J. Dudley, and P. Nicholls, *J. Chem. Soc.* (*A*), 1969, 2312.