Electronic Properties and Stereochemistry of the Bis(diethylenetriamine)-copper(II) Cation. Part 1. A Fluxional Elongated CuN_6 Chromophore

By **Mary Duggan, Brian J. Hathaway,* and John Mullane,** The Chemistry Department, University College, Cork, Ireland

The *X*-ray crystal structures of $[Cu(dien)_2]Cl_2{\cdot}H_2O$, $[Cu(dien)_2]Cl[ClO_4]$, $[Zn(dien)_2]Cl[ClO_4]$, and 38% copper-doped $[Zn(dien)_2]Cl[ClO_4]$, have been determined by photographic data for the first three complexes and diffractometer data for the doped system. All four complexes crystallise in the monoclinic space group $P2_1/c$ with $Z = 4$; the structures were solved by heavy-atom techniques and successive Fourier syntheses. The two copper(II) complexes involve elongated rhombic-octahedral $[Cu(dien)_2]^{2+}$ cations with the elongation along the N(1)–Cu–N(3) bond direction with a small but significant difference in the observed tetragonalities (0.853 and 0.835 respectively). The stereochemistry of the zinc(II) complex involves a compressed rhombic-octahedral ZnN_6 chromophore with the compression along the N(2)–Zn–N(5) bond direction. The structure of the 38% copper-doped $[Zn(dien)_2]Cl[ClO_4]$ was analysed as an average CuN_6/ZnN_6 chromophore and an attempt was made to solve this structure as disordered CuN_6 and ZnN_6 chromophores. The axes of the CuN_6 chromophore in $[Cu(dien)_2]Cl_2{\cdot}H_2O$ are aligned parallel, while those of $[Cu(dien)_2]Cl[ClO_4]$ are misaligned. The polycrystalline e.s.r. spectra of a series of copper-doped $[Zn(dien)_2]XY$ complexes are reported at both room and liquid-nitrogen temperature; all the spectra are consistent with an elongated rhombic-octahedral CuN_6 environment and the $g_\parallel$ and $A_\parallel$ factors show marked temperature dependence, with $\Delta A_\parallel$ varying from 8.9 to 36.0%. The temperature variation of the e.s.r. spectra of the copper-doped $[Zn(dien)_2]XY$ systems have been confirmed by single-crystal rotation e.s.r. data, consistent with the monoclinic space groups involved, and the *directions* of the g and A factors are shown to be temperature invariant. A correlation is established between the $\Delta A_\parallel$ values in the doped systems and the observed tetragonalities of the pure copper(II) complexes. The electronic reflectance spectra of the dilute and concentrated systems are shown to be independent of copper concentration and the polarised single-crystal electronic spectra of the doped system are assigned in a manner comparable to that of the pure copper(II) complex. The temperature-variable data are interpreted in terms of a fluxional model for the copper-doped $[Zn(dien)_2]XY$ systems and the data extrapolated to the concentrated copper(II) complex.

THE recent observation of significant temperature effects (fluxional behaviour) in the e.s.r. spectra of the copper-doped systems $Ba[Zn(O_2CH)_4]{\cdot}6H_2O$,[1] $[Zn(hfacac)_2(py)_2]$ [2] (where hfacac = hexafluoroacetylacetone and py = pyridine), and $K_2[Zn(OH_2)_6][SO_4]_2$ [3] and their description in terms of a pseudo-dynamic Jahn–Teller effect [4-6] in these low-symmetry crystals has suggested an examination of the electronic properties, and their variation with temperature, of the near-octahedral CuN_6 chromophore in some $[Cu(dien)_2]X_2$ complexes [7] and when these are doped into the corresponding $[Zn(dien)_2]X_2$ complexes as a diamagnetic host lattice (dien = diethylenetriamine). The crystal structures of $[Cu(dien)_2]Br_2{\cdot}H_2O$ [8] and $[Cu(dien)_2][NO_3]_2$ [9] have been previously reported along with that of $[Zn(dien)_2]Br_2{\cdot}H_2O$ [10] and monoclinic $[Zn(dien)_2][NO_3]_2$.[11,12] The present paper reports the crystal structures of $[Cu(dien)_2]Cl_2{\cdot}H_2O$, $[Cu(dien)_2]Cl[ClO_4]$, $[Zn(dien)_2]Cl[ClO_4]$, and an attempted crystal structure determination of 38% copper-doped $[Zn(dien)_2]Cl[ClO_4]$ as a disordered lattice. The electronic properties of these copper-doped $[Zn(dien)_2]XY$ systems are reported and interpreted in terms of a fluxional [3] elongated rhombic-octahedral CuN_6 chromophore.

EXPERIMENTAL

Preparation of Copper-doped Crystals.—The copper(II)-doped $[Zn(dien)_2]XY$ complexes were prepared by methods similar to those used for the preparation of the analogous pure copper or pure zinc complexes,[7] but using the appropriate ratio of copper : zinc salt to produce copper concentrations in the range 1—50%. Single crystals were prepared by recrystallisation of the polycrystalline samples from water or methanol solutions. All samples were characterised by microanalysis (Table 1) and their morphologies established by *X*-ray crystallographic precession techniques [Figure 1(*a*)—(*d*)]. In general the copper(II)-doped

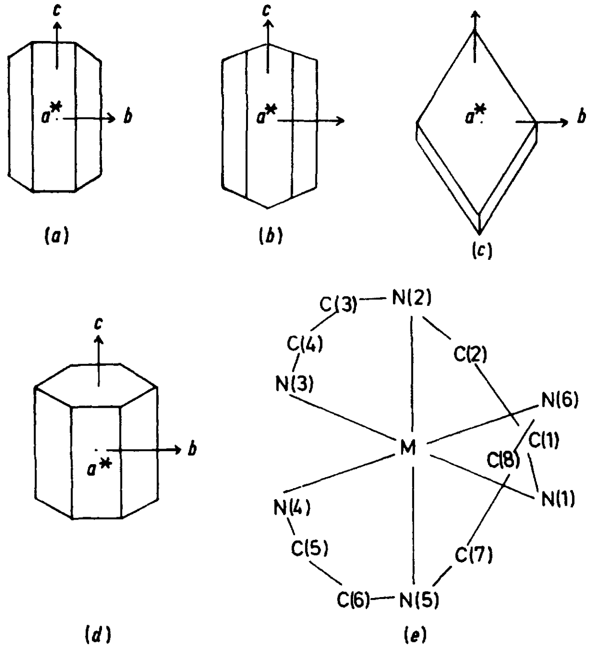


FIGURE 1 Crystal morphologies of the copper-doped $[Zn(dien)_2]$-XY systems, (*a*) X = Y = NO_3 monoclinic type I; (*b*) type II; (*c*) X = Y = $Cl{\cdot}0.5H_2O$ or $Br{\cdot}0.5H_2O$; (*d*) X = Cl, Y = ClO_4; and (*e*) the local molecular structure of the $[Cu(dien)_2]^{2+}$ and $[Zn(dien)_2]^{2+}$ cations and the atom-numbering scheme used

crystals corresponded in structure and morphology to those of the corresponding pure zinc(II) complexes,[11,12] except in the case of the monoclinic form of $[Zn(dien)_2][NO_3]_2$ where two different morphologies occurred with the doped complexes, type I agreed with that of the pure zinc complex, but type II, while having the same space group $P2_1/c$, had a related but slightly different morphology [Figure 1, (*a*) and (*b*)].

TABLE 1

Microanalytical data for the $[Cu(dien)_2]XY$ and $[Zn(dien)_2]XY$ complexes

Complex	Analysis (%) *				
	C	H	N	M	X
$[Cu(dien)_2]Cl[ClO_4]$	23.9	6.50	20.90	15.2	17.5
	(23.75)	(6.40)	(20.75)	(15.7)	(17.55)
$[Cu(dien)_2]Cl_2{\cdot}H_2O$	26.7	7.75	23.3	17.35	19.75
	(27.75)	(7.80)	(23.40)	(17.70)	(19.8)
$[Zn(dien)_2]Cl[ClO_4]$	23.45	6.30	20.80	15.90	17.3
	(23.60)	(6.4)	(20.65)	(16.1)	(17.45)

* Calculated values are given in parentheses.

Crystal Data.—The crystal and refinement data of $[Cu(dien)_2]Cl_2{\cdot}H_2O$ (1), $[Cu(dien)_2]Cl[ClO_4]$ (2), $[Zn(dien)_2]Cl[ClO_4]$ (3), and 38% copper-doped $[Zn(dien)_2]Cl[ClO_4]$ (4) are summarised in Table 2. The unit-cell parameters were determined from precession photographs and the intensity data were collected photographically using the equi-inclination Weissenberg technique for (1), (2), and (3). Five-film packs were used for each layer and the intensities were estimated spectrophotometrically using the S.R.C. Microdensitometer Service (Rutherford Laboratory). The data for (4) were collected on a Philips PW 1100 four-circle diffractometer, using graphite monochromatised Mo-K_α radiation; a θ—2θ scan mode was used and reflections with $3.0 < \theta < 32°$ in one quadrant were examined. A constant scan speed of 0.05° s^{-1} and a variable scan width of $(0.7 + 0.1 \tan \theta)°$ was used.

TABLE 2

Crystal and refinement data

Complex	(1) $[Cu(dien)_2]Cl_2{\cdot}H_2O$	(2) $[Cu(dien)_2]Cl[ClO_4]$	(3) $[Zn(dien)_2]Cl[ClO_4]$	(4) $[Cu_{0.38}Zn_{0.62}(dien)_2]$-$Cl[ClO_4]$
Molecular weight	358.54	404.54	406.37	405.67
Stoicheiometry	$C_8H_{28}Cl_2CuN_6O$	$C_8H_{26}Cl_2CuN_6O_4$	$C_8H_{26}Cl_2N_6O_4Zn$	$C_8H_{26}Cl_2Cu_{0.38}N_6O_4Zn_{0.62}$
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a(Å)	13.62(5)	9.23(5)	9.23(5)	9.230(2)
b(Å)	8.80(5)	13.92(5)	13.91(5)	13.814(2)
c(Å)	13.96(5)	14.65(5)	14.65(5)	14.709(12)
β(°)	102.7(5)	116.0(5)	116.0(5)	116.35(2)
Z	4	4	4	4
D_m(flotation)(g cm^{-3})	1.380	1.586	1.588	1.588
D_c (g cm^{-3})	1.458	1.588	1.595	1.578
Radiation	Cu-$K\alpha$, $\lambda = 1.541\,8$ Å	Cu-$K\alpha$, $\lambda = 1.541\,8$ Å	Cu-$K\alpha$, $\lambda = 1.541\,8$ Å	Mo-$K\alpha$, $\lambda = 0.710\,69$ Å
F(000)	747.88	836.0	840.00	838.27
μ(cm^{-1})	46.88	47.27	49.11	16.62
Data used	*h*, 0—7, *l*; *h*, *k*, 1—3	0—7, *k*, *l*; *h*, 1—2, *l*	0—7, *k*, *l*; *h*, 1—2, *l*	
Number of unique reflections	1, 508	740	760	3 289
Number of parameters varied	119	91	94	191
$R = (\Sigma\Delta/\Sigma\|F_o\|)$	0.058 8	0.061 7	0.056 2	0.034 7
$R' = (\Sigma\Delta w^{\frac{1}{2}}/\Sigma\|F_o\|w^{\frac{1}{2}})$	0.065 6	0.065 7	0.059 3	0.037 3
k	0.472 2	8.326 6	12.615 4	2.434 3
g	0.009 976	0.000 401	0.000 129	0.000 178
Maximum final shift to error	0.010	0.020	0.003	0.010
Residual electron density (e $Å^{-3}$)	0.94	0.54	0.53	0.050
Number of atoms anisotropic	9	1	1	21

Structure Solution and Refinement.—The structures of (1), (2), and (3) were solved using three-dimensional Patterson and Fourier techniques, using the crystallography program SHELX-76 (G. M. Sheldrick), with successive addition of atom positions to improve the phasing. The structures were refined by full-matrix least-squares refinement where the function minimised was $\Sigma w(|F_c| - |F_o|)^2$ until the final shift to error ratio for any parameter was less than 0.02 : 1. Calculated hydrogen-atom positions were used, with fixed C–H and N–H bond lengths of 1.08 Å (with a fixed temperature factor of 0.07 $Å^2$) and floated on the associated carbon- or nitrogen-atom positions; no hydrogens were included for the water molecule of (1). A refined weighting scheme was used, where $w = k/\{\sigma^2|F_o| + g|F_o^2|\}$; the final values of *k* and *g* in the refiment are in Table 2. Complex neutral scattering factors[13] were used for the non-hydrogen atoms, Lorentz and polarisation corrections were applied, but no correction was made for absorption. The data for (4) were handled slightly differently from those of (1)—(3), a Patterson synthesis yielded the same heavy-atom position to that of (2) and (3); consequently the atom positions of (2) were used as the initial input data for (4) with a mean structure factor ($f_m = 0.38f_{Cu^{II}} + 0.62f_{Zn^{II}}$) and the structure refined as above. An attempt was made to solve the data as a disordered structure[14] with two separate ZnN_6 and CuN_6 chromophores (weighted at 0.62 and 0.38 respectively) and although reasonable geometries were obtained (see later) this solution resulted in final maximum shift to error values of <0.4 and was considered not to converge satisfactorily. For this reason the disordered structure is not reported in detail and only the average structure is given.

As the final structures of the $[M(dien)_2]^{2+}$ cations in all four structures are comparable[8-12] and only differ in the detail of the anions present, a summary of the most important bond-length and bond-angle data is given in Table 3 and the detailed tables of the structure factors, atom positions, anisotropic temperature factors, calculated hydrogen-atom positions, bond lengths, bond angles, and some relevant mean planes are given in Supplementary Publication No. SUP 22708 (60 pp.).* Figure 1(*e*) shows the local molecular structure of the $[M(dien)_2]^{2+}$ cation and the atom-numbering scheme used.

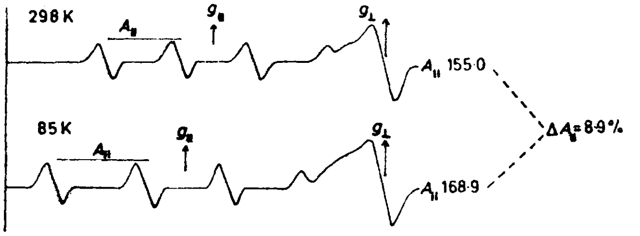


FIGURE 2 Polycrystalline e.s.r. spectra of a typical 1% copper-doped $[Zn(dien)_2]XY$ system at room temperature and at liquid-nitrogen temperature

TABLE 3

A summary of the more important bond lengths and angles for (1) $[Cu(dien)_2]Cl_2{\cdot}H_2O$, (2) $[Cu(dien)_2]Cl(ClO_4]$, (3) $[Zn(dien)_2]Cl[ClO_4]$, and (4) 38% copper-doped $[Zn(dien)_2]Cl[ClO_4]$ (average structure)

	(1)	(2)	(3)	(4)
(*a*) Bond lengths				
M–N(1)	2.372(7)	2.386(14)	2.232(15)	2.297(5)
M–N(2)	2.036(8)	2.037(13)	2.111(15)	2.099(5)
M–N(3)	2.466(6)	2.516(13)	2.297(15)	2.386(5)
M–N(4)	2.118(6)	2.089(13)	2.220(15)	2.169(5)
M–N(5)	2.034(8)	2.025(13)	2.218(15)	2.097(4)
M–N(6)	2.073(6)	2.036(13)	2.183(15)	2.143(5)
(*b*) Bond angles				
N(1)–M–N(2)	79.3(3)	79.6(6)	80.4(6)	79.2(2)
N(2)–M–N(3)	78.2(3)	77.8(6)	78.4(6)	78.7(2)
N(1)–M–N(3)	156.5(3)	155.3(5)	156.2(5)	155.4(1)
N(4)–M–N(5)	83.1(3)	82.0(6)	78.8(6)	81.0(2)
N(5)–M–N(6)	83.5(3)	83.7(6)	80.2(6)	80.6(2)
N(4)–M–N(6)	164.4(2)	162.0(6)	157.2(5)	159.1(1)
N(2)–M–N(5)	178.4(2)	177.8(5)	175.4(5)	176.3(1)

TABLE 4

Electron spin resonance parameters for copper-doped $[Zn(dien)_2]XY$ systems at room temperature and liquid-nitrogen temperature

X	Y	T (K)	$g_\perp$	$g_\parallel$	$A_\parallel$ ($\times 10^4$ cm^{-1})	$\Delta A_\parallel$ (%)
Cl	ClO_4	291	2.052	2.228	155.0	
		85	2.042	2.233	168.9	8.9
Cl	BF_4	291	2.040	2.221	155.0	
		85	2.035	2.237	170.6	10.1
$Cl{\cdot}0.5H_2O$	$Cl{\cdot}0.5H_2O$	291	2.048	2.212	142.6	
		85	2.050	2.239	168.0	17.8
$Br{\cdot}0.5H_2O$	$Br{\cdot}0.5H_2O$	291	2.033	2.204	127.3	
		85	2.035	2.236	155.3	22.0
NO_3	NO_3	291	2.046	2.216	132.4	
[monoclinic type I]		85	2.046	2.226	170.5	28.8
I	I	291	2.054	2.193	129.8	
		85	2.051	2.237	168.0	29.5
Cl	NO_3	291	2.053	2.202	129.8	
		85	2.047	2.233	170.6	31.4
Br	NO_3	291	2.054	2.205	124.5	
		85	2.049	2.229	169.3	36.0

Electronic Properties.—These were recorded as previously described.[5,15]

Table 4 lists the polycrystalline e.s.r. spectral results of a series of copper-doped $[Zn(dien)_2]XY$ complexes measured at room and liquid-nitrogen temperature with the temperature variation indicated by the percentage change in the $A_\parallel$ values. Figure 2 illustrates typical e.s.r. spectra for these systems {copper-doped $[Zn(dien)_2]Cl[ClO_4]$}, demonstrating how the spectra change with temperature. Figure 3 shows the detailed temperature variation of the g and A factors of copper-doped $[Zn(dien)_2]Br_2{\cdot}H_2O$ and the $A_\parallel$ factors for $[Cu(dien)_2]Cl_2{\cdot}H_2O$ and $[Cu(dien)_2]Cl[ClO_4]$, the tabulated data for which is included in SUP 22708. Table 5 lists the room-temperature single-crystal g and A factors for the copper-doped $[Zn(dien)_2]Cl_2{\cdot}H_2O$ and $[Zn(dien)_2]Cl[ClO_4]$ systems along with their direction cosines and those of the Cu–N directions. Table 6 lists the polycrystalline g factors for some *concentrated* copper(II) complexes measured at room and liquid-nitrogen temperature. Table 7 lists the polycrystalline electronic reflectance spectra of some 10% doped and concentrated $[Cu(dien)_2]XY$ complexes.[16] Figure 4 illustrates the polarised single-crystal electronic spectra of the copper-doped $[Zn(dien)_2]Br_2{\cdot}H_2O$ system.

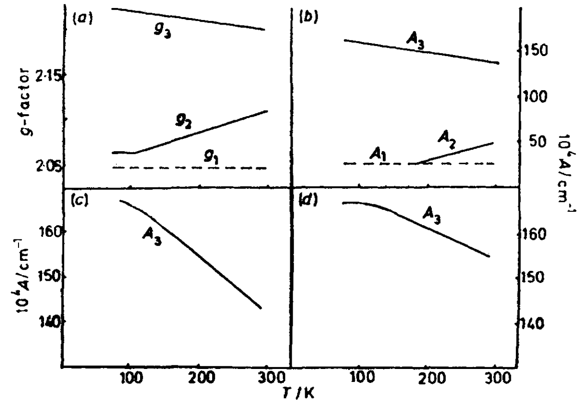


FIGURE 3 Polycrystalline e.s.r. data as a function of temperature: (*a*) copper-doped $[Zn(dien)_2]Br_2{\cdot}H_2O$, g factors; (*b*) copper-doped $[Zn(dien)_2]Br_2{\cdot}H_2O$, A factors; (*c*) 10% copper-doped $[Zn(dien)_2]Cl_2{\cdot}H_2O$, A factors; and (*d*) 10% copper-doped $[Zn(dien)_2]Cl[ClO_4]$, A factors

DISCUSSION

Description of the Crystal Structures.—All four structures consist of non-centrosymmetric $[M(dien)_2]^{2+}$ cations

---

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

and ionic anions with no evidence for co-ordination of the metal by the anions or by the water molecule in (1). In the cations the diethylenetriamine ligands co-ordinate as planar tridentate ligands, as found previously [8-12] for this ligand when bonded to the copper(II) ion, with no exceptional bond lengths or angles. In (1) and (2) the CuN_6 chromophore has an elongated rhombic-octahedral stereochemistry, with the elongation along the N(1)-Cu-N(3) direction.[8] Consequently, the two dien ligands are inequivalent in their bonding role as observed previously for $[Cu(dien)_2]Br_2{\cdot}H_2O$.[8] The tetragonalities of the CuN_6 chromophore of (1) and (2) are comparable to those listed previously, Table 8. In the ZnN_6 chromophores the dien ligands are more nearly equivalent in their mode of co-ordination, and the stereochemistry is better described as compressed rhombic-octahedral,[10-12] but with the compression along the short N(2)-Cu-N(5) bond directions, consistent with the spherical symmetry of the d^{10} configuration of the zinc(II) ion and the constraints imposed by the ' bites ' of the dien ligands. In (2), (3), and (4) the perchlorate ion occupies a general position and no unusual bond lengths or angles are observed.[17]

TABLE 5

Copper-doped $[Zn(dien)_2]XY$ systems: single-crystal data, g and A factors, R values at room and liquid-nitrogen temperatures, direction cosines of g factors, and the local molecular direction of CuN_6 chromophores

	$[Zn(dien)_2]Cl[ClO_4]$		$[Zn(dien)_2]Cl_2{\cdot}H_2O$	
	291 K	85 K	291 K	85 K
g_1	2.0460	2.0456	2.0410	2.0381
g_2	2.0922	2.0540	2.1244	2.0988
g_3	2.2389	2.2446	2.2302	2.2416
$10^4\ A_1/cm^{-1}$	*ca.* 30	*ca.* 30	*ca.* 26	*ca.* 26
$10^4\ A_2/cm^{-1}$	75	40	75	70
$10^4\ A_3/cm^{-1}$	155	168	143	168
ΔA_3 (%)		8.4		17.5
$R\left\{\frac{g_2 - g_1}{g_3 - g_2}\right\}$	0.32	0.45	0.79	0.43

Direction cosines

	a^*	b	c	a^*	b	c
g_1	0.866 0	0.121 9	0.422 6	0.087 2	0.992 5	0.069 4
g_2	0.173 6	0.615 7	−0.819 2	−0.906 3	0.121 9	0.422 6
g_3	0.258 8	−0.788 0	−0.707 1	−0.422 6	0.121 8	−0.906 3
N(2)	0.938 7	0.112 1	0.325 9	0.094 7	0.994 2	0.051 7
N(4)-N(6)	0.155 0	0.620 8	−0.768 5	−0.925 1	0.055 5	0.375 7
N(1)-N(3)	0.278 9	−0.746 2	−0.604 5	−0.399 2	0.062 0	−0.914 8

TABLE 6

The polycrystalline g factors of $[Cu(dien)_2]Cl_2{\cdot}H_2O$ and $[Cu(dien)_2]Br_2{\cdot}H_2O$ at (*a*) room temperature and (*b*) liquid nitrogen temperature, with the corresponding polycrystalline g factors of the dilute copper-doped $[Zn(dien)_2]X_2$ systems in parentheses

		(*a*)	(*b*)	$\Delta g_{\parallel}$
$[Cu(dien)_2]Cl_2{\cdot}H_2O$	g_1	2.050 (2.041)	2.049 (2.038)	
	g_2	2.070 (2.124)	2.090 (2.099)	
	g_3	2.210 (2.212)	2.226 (2.329)	0.016 (0.027)
$[Cu(dien)_2]Br_2{\cdot}H_2O$	g_1	2.043 (2.033)	2.043 (2.035)	
	g_2	2.097 (2.113)	2.065 (2.065)	
	g_3	2.213 (2.204)	2.230 (2.236)	0.017 (0.032)

The structure of 38% copper-doped $[Zn(dien)_2]Cl[ClO_4]$ is very similar to those of the pure copper(II) and zinc(II) complexes, except that the average structure of the copper-doped ZnN_6 chromophore involves intermediate bond lengths (Figure 5). Included in Figure 5 are the bond lengths for the CuN_6 and ZnN_6 chromophores of the disordered solution [14] from the data for the 38% copper-doped $[Zn(dien)_2]Cl[ClO_4]$ crystals. Despite the failure of this model to fully converge, the stereochemistries of the separate chromophores are closely comparable to those of the corresponding pure zinc(II) and copper(II) complexes. This suggests that within the isomorphous series of copper-doped $[Zn(dien)_2]Cl[ClO_4]$ complexes the CuN_6 chromophore assumes the stereochemistry of concentrated $[Cu(dien)_2]Cl[ClO_4]$ and is not seriously modified by the compressed stereochemistry of the ZnN_6 chromophore of the diamagnetic host lattice even at this 38% copper(II) concentration.

In the monoclinic space group of (1) the CuN_6 chromophores are aligned virtually parallel [$2\alpha = 14°$ (ref. 18); Table 5] with the elongated N(1)-Cu-N(3) direction lying in the *ac* plane and inclined at an angle of 30° to the *c* axis, similar to the situation in $[Cu(dien)_2]Br_2{\cdot}H_2O$,[8] with which (1) is isomorphous and nearly isostructural. In $[Zn(dien)_2][NO_3]_2$ [11,12] the ZnN_6 chromophores are slightly misaligned ($2\alpha = 10°$) while in (2), (3), and (4) there is almost complete misalignment (Table 5; $2\alpha = 75°$).

Electronic Properties.—The e.s.r. spectra of the copper-doped system (see Table 4 and Figure 3) are typical [18] of an elongated rhombic-octahedral CuN_6 environment, namely $g_{\parallel} \gg g_{\perp}$ ($g_1 \approx g_2$) > 2.0, for the copper(II) ion diluted in a diamagnetic host lattice. Four copper hyperfine lines [19] are associated with the $g_{\parallel}$ value with $A_{\parallel}$ *ca.* 120×10^{-4}—170×10^{-4} cm^{-1} but no hyperfine structure is observed on $g_{\perp}$, as $A_{\perp}$ is probably less than 25×10^{-4} cm^{-1}. The spectra are consistent with the known stereochemistry of the elongated CuN_6 chromophore of the three corresponding pure copper(II) complexes, $[Cu(dien)_2]Br_2{\cdot}H_2O$, $[Cu(dien)_2]Cl_2{\cdot}H_2O$, and $[Cu(dien)_2]Cl[ClO_4]$ and are *not* consistent with the compressed rhombic-octahedral stereochemistry [18] of the ZnN_6 chromophores of the host lattices.

TABLE 7

Electronic reflectance data (cm^{-1}) for (*a*) some 10% copper-doped $[Zn(dien)_2]XY$ complexes and (*b*) the corresponding pure copper(II) complexes, with relative intensities in parentheses

(*a*) $[Zn(dien)_2]Cl[ClO_4]$	16 100 (0.9)	9 900 (0.6)
$[Zn(dien)_3]Cl_2{\cdot}H_2O$	16 100 (0.9)	9 600 (0.6)
$[Zn(dien)_2]Br_2{\cdot}H_2O$	16 100 (0.9)	9 500 (0.6)
(*b*) $[Cu(dien)_2]Cl[ClO_4]$	16 100 (0.9)	9 900 (0.6)
$[Cu(dien)_2]Cl_2{\cdot}H_2O$	16 100 (0.9)	9 600 (0.6)
$[Cu(dien)_2]Br_2{\cdot}H_2O$	16 100 (0.9)	9 500 (0.6)

The e.s.r. spectra change significantly with temperature; [1-3] as the temperature is lowered the $g_{\parallel}$ and $A_{\parallel}$ values increase, while $g_{\perp}$ shows a smaller decrease [except in the case of copper-doped $[Zn(dien)_2]Cl_2{\cdot}H_2O$]. These temperature changes are even more significant in the full single-crystal e.s.r. data of copper-doped $[Zn(dien)_2]Br_2{\cdot}H_2O$, Figures 3(*a*) and 3(*b*), and in the data for copper-doped $[Zn(dien)_2]Cl[ClO_4]$ and $[Zn(dien)_2]Cl_2{\cdot}H_2O$ where the $A_{\parallel}$ values only are reported, Figures 3(*c*) and 3(*d*). In the single-crystal data the g_3 and A_3 values increase with decreasing temperature, g_2 and A_2 decrease, and g_1 and A_1 show no significant temperature variation.

TABLE 8

The tetragonalities (T) for the $[M(dien)_2]^{2+}$ cation (T = mean in-plane bond distance/mean out-of-plane distance)

(*a*) Copper(II)	Elongated N(1)–Cu–N(3)
$[Cu(dien)_2]Br_2{\cdot}H_2O$	0.835
$[Cu(dien)_2]Cl_2{\cdot}H_2O$	0.853
$[Cu(dien)_2]Cl[ClO_4]$	0.860
(*b*) Zinc(II)	Compressed N(2)–Zn–N(5)
$[Zn(dien)_2][BF_4]_2$	1.054 1
$[Zn(dien)_2]Cl[ClO_4]$	1.053 5
$[Zn(dien)_2]Br_2{\cdot}H_2O$ (isomorphous with $Cl_2{\cdot}H_2O$)	1.045 2
$[Zn(dien)_2][NO_3]_2$* (orthorhombic)	1.040 0
$[Zn(dien)_2][NO_3]_2$ (monoclinic)	1.031 7
	(1.04 3)

* Ref. 12.

The copper-doped system yielded typical [19] angular variation of the single-crystal e.s.r. spectra consistent with the monoclinic systems involved, the precise details of which depend very much on the alignment of the copper-doped ZnN_6 chromophore present. In copper-doped $[Zn(dien)_2]X_2{\cdot}H_2O$ (X = Cl or Br), where the chromophores are virtually aligned,[8] only four hyperfine lines are observed in the rotational e.s.r. spectra (except in the direction of g_1 where an almost isotropic signal was observed), consistent with only one magnetic site. Table 5 lists the direction cosines for the observed g and A factors along with the direction cosines of the appropriate copper-doped Zn–N directions. The g values clearly lie close to the bonding directions and establish the presence of an approximately $d_{x^2-y^2}$ ground state for these copper-doped $[Zn(dien)_2]X_2{\cdot}H_2O$ systems, consistent with the data previously determined [16] for the pure $[Cu(dien)_2]Br_2{\cdot}H_2O$, with g_1 associated with the N(2)–N(5) direction, g_2 with the N(4)–N(6) direction, and g_3 with the N(1)–N(3) direction. Corresponding data were also obtained for the copper-doped $[Zn(dien)_2]Cl[ClO_4]$ system, Table 5, but due to the gross misalignment of the CuN_6 chromophores, two magnetic sites are present misaligned by approximately $2\alpha = 75°$ and four e.s.r. lines only are observed in the *ac*-plane and in the unique *b*-axis spectra; elsewhere more than four lines were observed associated with the two magnetic sites present. Nevertheless, the data of Table 5 indicate that the g factors of the two separate sites correspond with the Cu–N directions of the copper-doped ZnN_6 chromophores. In *all* the single-crystal data although the g and

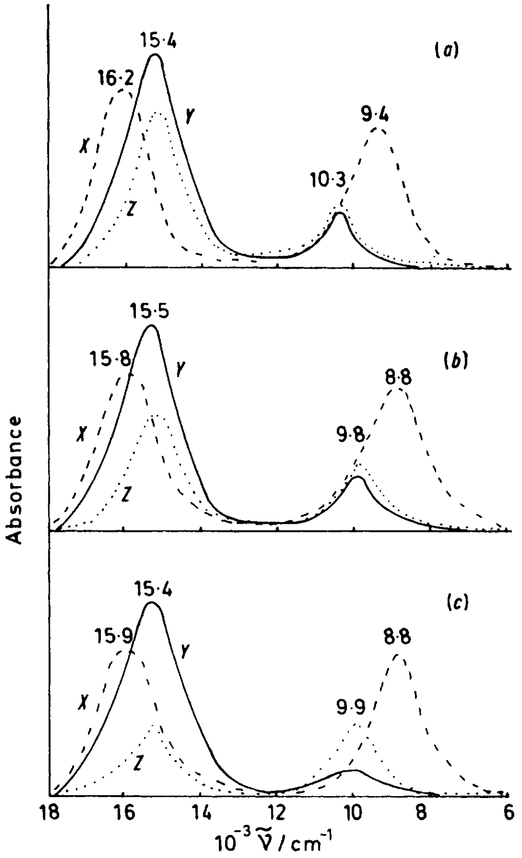
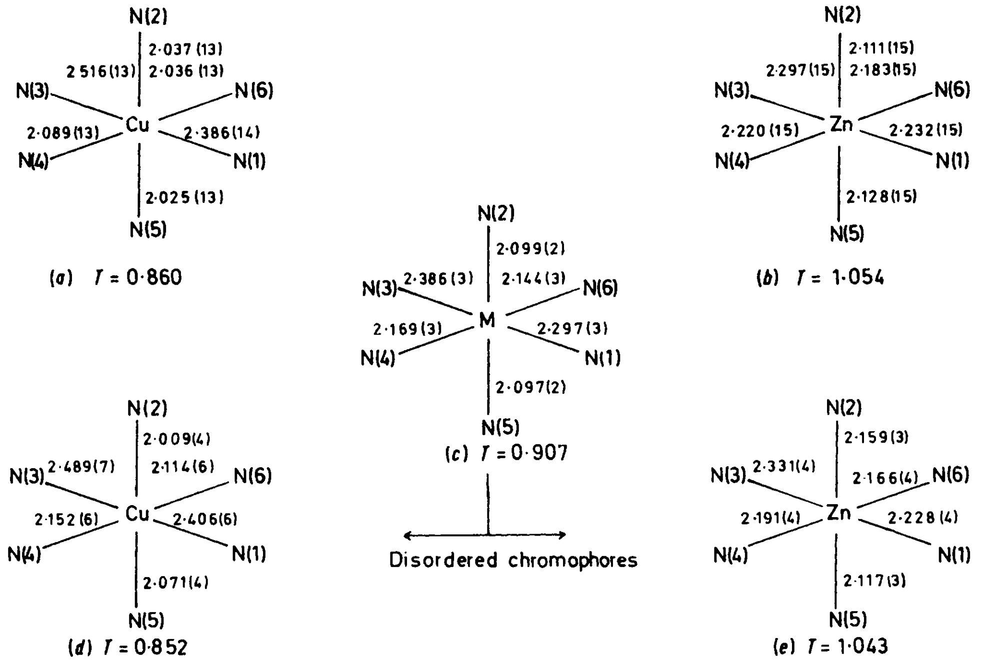


FIGURE 4 Polarised single-crystal electronic spectra (ref. 16) of (*a*) copper-doped $[Zn(dien)_2]Br_2{\cdot}H_2O$; (*b*) copper-doped $[Zn(dien)_2][NO_3]_2$ monoclinic type I; and (*c*) $[Cu(dien)_2]Br_2{\cdot}H_2O$. See ref. 16 for *x*, *y*, and *z* notation

A factors may vary (Table 5) with temperature, their directions are temperature *invariant.*

In all of the room-temperature and low-temperature polycrystalline and single-crystal e.s.r. spectra of the dilute copper-doped systems no evidence for nitrogen hyperfine splitting was observed despite the presence of CuN_6 chromophores. Table 6 reports the temperature variation of the polycrystalline e.s.r. spectra of the pure $[Cu(dien)_2]Br_2{\cdot}H_2O$ and $[Cu(dien)_2]Cl_2{\cdot}H_2O$ complexes; in both complexes g_3 increases with decreasing temperature and g_1 is almost temperature invariant, the position of g_2 is much less certain but decreases in the former but not in the latter. This temperature variation parallels the variation of the g factors in the dilute systems (except for the behaviour of the much less certain g_2) and confirms that the temperature variation of at least g_3 and g_1 is independent of the copper(II)-ion concentration.



(*a*) *T* = 0·860

(*b*) *T* = 1·054

(*c*) *T* = 0·907

(*d*) *T* = 0·852

(*e*) *T* = 1·043

FIGURE 5 Local molecular structures of the MN_6 chromophores of 1—100% copper-doped $[Zn(dien)_2]Cl[ClO_4]$. (*a*) 100% Cu; (*b*) 100% Zn; (*c*) average $Cu_{0\cdot38}:Zn_{0\cdot62}$; (*d*) disordered 38% CuN_6; and (*e*) disordered 62% ZnN_6

The electronic spectra of all these copper-doped $[Zn(dien)_2]XY$ and $[Cu(dien)_2]XY$ systems are very similar (Table 7) with two bands,[16] the more intense at 16 100 cm^{-1} and the less intense at 9 500—9 900 cm^{-1} and only the latter varies slightly with the anion present. For the systems of Table 7 the spectra were *independent* of the copper(II)-ion concentration and showed little variation with temperature (<200 cm^{-1} to higher energy). The polarised single-crystal electronic spectra of the copper-doped $[Zn(dien)_2]Br_2{\cdot}H_2O$ system, Figure 4(*a*), was identical with that observed in the corresponding $[Cu(dien)_2]Br_2{\cdot}H_2O$ complex,[16] Figure 4(*c*), except for some small but significant differences, in the energy of the lower-energy bands in particular, and the relatively higher intensity of the *z*-polarised band at 15 400 cm^{-1} in the dilute system. The polarised single-crystal spectrum, Figure 4(*b*), of the nearly aligned copper-doped $[Zn(dien)_2][NO_3]_2$ monoclinic system is also like that of the bromide and suggests that the CuN_6 environments of the two dilute systems are very similar, in spite of the failure to isolate crystals of the pure monoclinic $[Cu(dien)_2][NO_3]_2$ complex.[12] In view of the similarity of the polarised spectra of the dilute and concentrated $[Cu(dien)_2]Br_2{\cdot}H_2O$ systems the spectra may be assigned in the manner previously reported for the pure copper(II) complex,[16] the results being listed in Table 9.

Fluxional Model.—The marked temperature variation of the e.s.r. spectra of these copper-doped systems can be understood in terms of the presence of fluxional behaviour [1-3] in the CuL_6 chromophore as recently described for the copper-doped $Ba[Zn(O_2CH)_4]{\cdot}6H_2O$, $[Zn(hfacac)_2(py)_2]$, and $K_2[Zn(OH_2)_6][SO_4]_2$ systems. All of these systems occur in lower than cubic symmetry and the CuL_6 chromophores will be subject to the pseudo-dynamic Jahn–Teller effect [4-6] to varying degrees. Under the effect of the low crystal symmetry the observed CuL_6 chromophore stereochemistry at a particular temperature is determined by the relative thermal population of the three available potential-energy wells, each corresponding to an elongated rhombic-octahedral stereochemistry misaligned in three mutually perpendicular directions and related by the three-fold axis of the parent octahedron (Figure 6). When only the lowest potential-energy well, I, is occupied a static elongated chromophore is observed which is non-temperature variable, but if the next lowest potential-energy well, II, is low enough in energy ($\Delta E < kT$), then partial thermal population will occur and the observed stereochemistry will be a mean of the elongated rhombic-octahedral stereochemistries of I and II, weighted according to their thermal population. In addition the observed stereochemistry (and the associated e.s.r. spectra) will be temperature variable, a result that has been predicted [20,21] and confirmed by the recent low-temperature crystal structure [22] of $[NH_4]_2[Cu(OH_2)_6][SO_4]_2$ (see Table 10) where the elongated rhombic-octahedral stereochemistry of the room-temperature structure shows a marked increase in the elongation present at a temperature of *ca.* 150 K, which parallels marked changes in the e.s.r. spectra.[23]

TABLE 9

The one-electron energy level assignment (cm^{-1}) of (*a*) copper-doped $[Zn(dien)_2]Br_2 \cdot H_2O$, (*b*) copper-doped $[Zn(dien)_2][NO_3]_2$ monoclinic type I, (*c*) pure $[Cu(dien)_2]Br_2 \cdot H_2O$

Assignment	(*a*)	(*b*)	(*c*)
$d_{z^2} \rightarrow d_{x^2-y^2}$	9 400	8 800	8 800
$d_{z^2} \rightarrow d_{x^2-y^2}$	10 300	9 800	9 900
$d_{z^2} \rightarrow d_{x^2-y^2}$	15 400	15 500	15 400
$d_{z^2} \rightarrow d_{x^2-y^2}$	15 200	15 800	15 900

In the copper-doped $[Zn(dien)_2]XY$ system the three elongation axes are along the N(1)–Cu–N(3), N(4)–Cu–N(6), and N(2)–Cu–N(5) bonding directions; of these the last one corresponds to the highest energy as it involves the most energetically unfavourable elongation against the constraint of the methylene links of the dien ligand. The two elongations involving the terminal nitrogen atoms are comparable, energetically, and of lower energy, with lattice-packing forces determining that I lies lowest, with II to slightly higher energy, but thermally accessible. The greatest elongation (and lowest tetragonality, T) will occur when only I is occupied and will correspond to the least variation of $g_{\parallel}$ or $A_{\parallel}$ with temperature. If $\Delta A_{\parallel}$, Table 4, is taken as a measure of the variation of $A_{\parallel}$ with temperature, the larger $\Delta A_{\parallel}$, the greater the fluxional behaviour present, the higher the thermal population of II, and the higher the observed tetragonality for the CuN_6 chromophore in the corresponding pure copper(II) complex. Where this data is available, Figure 7, it shows a reasonable correlation between the observed tetragonality of the pure $[Cu(dien)_2]XY$ complexes and the corresponding value of $\Delta A_{\parallel}$ in the dilute systems, and suggests that the small differences in the observed tetragonalities of these three complexes are real differences and arise from the inherent differences in fluxional behaviour due to different crystal-packing effects. The maximum value of g_3 and A_3 and the minimum value of g_2 and A_2 will occur when only I is occupied, *i.e.* at low temperature (Figure 6); with increasing thermal occupation of II the values of g_3 and A_3 will be lowered and those of g_2 and A_2 will increase, while g_1 and A_1 will remain temperature invariant. The fluxional model for the temperature variation of the e.s.r. spectra of these copper-doped systems is also consistent with the absence of any change in direction of the measured g values with change in temperature. This arises due to the correspondence of the direction of the separate g factors of the two 90° misaligned chromophores in the potential wells I and II such that only the magnitudes of the average g factors are temperature variable and not their directions. While the above $\Delta A_{\parallel}$ values, Table 4, give a measure of

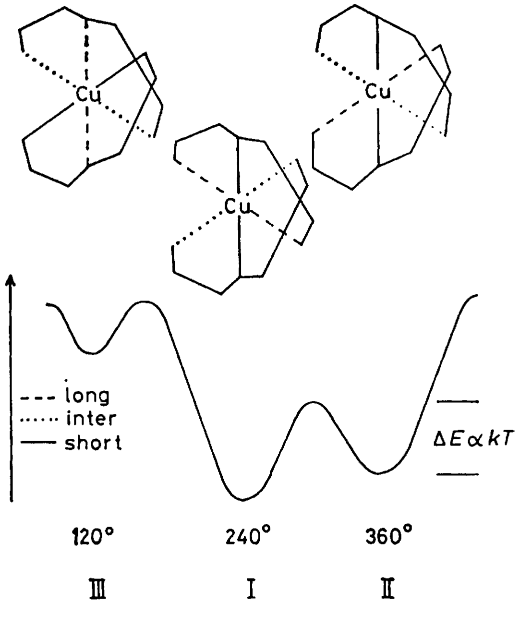


FIGURE 6 Potential-energy diagram for the copper-doped $[Zn(dien)_2]XY$ systems, elongated rhombic octahedral

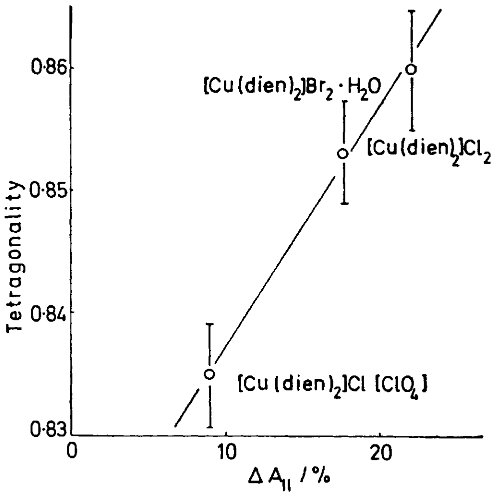


FIGURE 7 Plot of the tetragonality (T) of $[Cu(dien)_2]XY$ complexes against $\Delta A_{\parallel}$, measured on the corresponding polycrystalline samples (see Table 4)

TABLE 10

The Cu–O bond distances of $[NH_4]_2[Cu(OH_2)_6][SO_4]_2$ at room temperature, 298 K, and at *ca.* 150 K

	298 K	*ca.* 150 K
Cu–O(7)	2.219(5)	2.30(1)
Cu–O(8)	2.095(5)	2.02(1)
Cu–O(9)	1.961(5)	1.96(1)

the increasing fluxional behaviour of the different copper-doped systems it has not been possible to estimate the ΔE values of Figure 6 as the data of Figure 3 suggests that the minimum of the temperature variation has not been reached even at the temperature of liquid nitrogen, and the g and A factors associated with the purely static CuN_6 stereochemistry are not available.

The lack of variation in the energies of the electronic spectra of the copper-doped systems with concentration does suggest that there is, at most, only a small variation in the basic elongated rhombic-octahedral CuN_6 stereochemistry. The association of the differing tetragonalities with small differences in the extent of fluxional behaviour suggests that the electronic spectra are very insensitive to differences in stereochemistry which must be locked in by the bite of the dien ligand, with crystal-packing factors modifying this only slightly from one lattice to another. The presence of fluxional behaviour will have little effect on the energies of the electronic transitions as these are relatively fast (10^{-13} s) compared with the vibrations of the CuN_6 chromophore (10^{-12} s). Consequently, the electronic transitions will correspond in energy to the extrema of the molecular vibrations associated with the vibronic mechanism, a factor which is consistent with the similarity of the polarised single-crystal electronic spectra of the concentrated and dilute copper-doped $[Zn(dien)_2]Br_2 \cdot H_2O$ systems (Figure 4).

It is relevant to ask whether the extent of fluxional behaviour is the same or different in concentrated and dilute copper-doped systems. The differences in the electronic spectra are minor and only in the aligned crystal system of the chloride and bromide complexes are the g factors (but not the A factors) similar in the concentrated and dilute form, and their separate variations with temperature determinable ($\Delta g_{\parallel}$) (Table 6). While the $\Delta g_{\parallel}$ values for the chloride and bromide are comparable, there is a significant difference between those of the concentrated and the dilute complexes, with the difference in the dilute complexes larger by a factor of two. This would suggest that the fluxional effect in the dilute systems may be greater than in the pure complexes, where the close proximity of like $[Cu(dien)_2]^{2+}$ cations would limit[24] the freedom of the cation to undergo independent fluxional behaviour. This is also consistent with the earlier observation[12] that the copper(II) ion readily distorts to give an elongated rhombic-octahedral stereochemistry which is independent of the compressed rhombic-octahedral stereochemistry of the ZnN_6 chromophore of the host lattice. For this reason, care should be exercised in equating the properties of the copper(II) ion diluted into a diamagnetic host lattice with those of the concentrated complex, even when the parent complexes are isomorphous, unless there is clear *electronic* evidence that they correspond. For the same reason it would be equally unwise to equate the local stereochemistry of a copper(II) ion in a doped system with the geometry of the host lattice.[25]

The term 'Plasticity effect'[24] has been introduced recently to describe the ability of the copper(II) ion to generate distortion isomers having the same empirical formulae but slightly different static local molecular stereochemistries and, corresponding slightly different electronic properties. This concept has been extended recently[26] to the formation of cation-distortion isomers in the series $[Cu(dien)(bipyam)]X_2$ [$X = NO_3$; $ClO_4 \cdot 0.5H_2O$, or $Cl \cdot H_2O$; bipyam = bis(2-pyridyl)amine] in which the CuN_5 chromophore varies from a distorted trigonal-bipyramidal to a distorted square-pyramidal stereochemistry, but each with a *static* local molecular stereochemistry. The three complexes $[Cu(dien)_2]XY$, ($X = Cl$, $Y = ClO_4$; $X = Y = Cl \cdot 0.5H_2O$; and $X = Y = Br \cdot 0.5H_2O$) also represent a series of cation-distortion isomers in which the rhombic-octahedral CuN_6 chromophore increases its apparent tetragonality from 0.835 to 0.860, a change that is associated not with a variation in a *static* stereochemistry but with a change in the *fluxional* properties of the CuN_6 chromophore. Consequently, while the existence of distortion isomers[24] (as well as cation- or anion-distortion isomers[26]) may be associated with the plasticity effect of the copper(II) ion,[24] the isomers may be observed with either static or fluxional stereochemistries.

We thank the Department of Education for the award of a grant (to M. D. and J. M.), the use of SHELX-76 *X*-ray crystallographic programs (Dr. G. Sheldrick, Cambridge University), the use of computing facilities (Computer Bureau, U.C.C.), the S.R.C. Microdensitometer Service, Harwell (Dr. M. Elder), for intensity estimation of the photographic data used [complexes (1), (2), and (3)], help in data collection [complex (4)] by Drs. P. G. Owston and M. McPartlin (The Chemistry Department, The Polytechnic of North London, Holloway), and the Microanalysis Section (U.C.C.) for analyses.

[9/731 *Received, 11th May,* 1979]

REFERENCES

[1] T. Ramasubba Reddy and R. Srinivasan, *Phys. Letters*, 1966, **22**, 143.

[2] J. Pradilla-Sorzano and J. P. Fackler, *Inorg. Chem.*, 1973 **12**, 1182.

[3] B. L. Silver and D. Getz, *J. Chem. Phys.*, 1974, **61**, 638.

[4] F. S. Ham, *Phys. Rev.*, 1968, **166**, 307.

[5] M. C. M. O'Brien, *Proc. Roy. Soc.*, 1964, **A281**, 323.

[6] I. B. Bersuker, *Co-ordination Chem. Rev.*, 1975, **14**, 357.

[7] M. J. Bew, B. J. Hathaway, and R. J. Fereday, *J.C.S. Dalton*, 1972, 1229.

[8] F. S. Stephens, *J. Chem. Soc.* (*A*), 1969, 2233.

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

[10] P. G. Hodgson and B. R. Penfold, *J.C.S. Dalton*, 1974, 1870.

[11] M. Zocchi, A. Albinati, and G. Tieghi, *Cryst. Structure Comm.*, 1972, **1**, 135.

[12] J. Mullane, Ph.D. Thesis, University College, Cork, 1975.

[13] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104; D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

[14] R. M. Clay, J. Murray-Rust, and P. Murray-Rust, *Acta Cryst.*, 1976, **B32**, 111.

[15] B. J. Hathaway, P. Nicholls, and D. Bernard, *Spectrovision*, 1969, **22**, 4.

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

[17] B. T. Kilbourne, R. R. Ryan, and J. D. Dunitz, *J. Chem. Soc.* (*A*), 1969, 2407.

[18] B. J. Hathaway and D. E. Billing, *Co-ordination Chem. Rev.*, 1970, **5**, 142.

[19] B. A. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, 1970, **13**, 135.

[20] B. J. Hathaway, Autumn Meeting of the Chemical Society, Crystallography Group, Sheffield, 1976.

[21] M. A. Hitchman and T. D. Waite, *Inorg. Chem.*, 1976, **15**, 2150, 2155; M. A. Hitchman, *J. Chem. Phys.*, 1978, **68**, 3425.

[22] M. Duggan, A. Murphy, and B. J. Hathaway, *Inorg. Nuclear Chem. Letters*, 1979, **15**, 150.

[23] F. E. Mabbs and J. K. Porter, *J. Inorg. Nuclear Chem.*, 1973, **35**, 3219.

[24] J. Gazo, I. B. Bersuker, J. Garaj, M. Kabesova, J. Kohout, H. Langfelderova, M. Melnik, M. Seraton, and F. Valach, *Co-ordination Chem. Rev.*, 1976, **19**, 253.

[25] A. Bencini, I. Bertini, D. Gatteschi, and A. Scozzafava, *Inorg. Chem.*, 1978, **17**, 3194.

[26] N. Ray, L. Hulett, R. Sheahan, and B. J. Hathaway, *Inorg. Nuclear Chem. Letters*, 1978, **14**, 305.