Crystal and Molecular Structures of μ-Oxalato-di[bisethylenediamine-nickel(II)] Dinitrate, μ-Oxalato-bis[di-(2-aminoethyl)aminecopper(II)] Diperchlorate, and μ-Oxalato-bis[di-(3-aminopropyl)aminezinc(II)] Diperchlorate

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Crystal and molecular structures of the title compounds are reported. In each the complex cation is dimeric with the planar oxalate group acting as a bridge by forming five-membered chelate rings with two metal centres. Coördination geometries are approximately octahedral in the nickel compound (I), square pyramidal in the copper compound (II) (oxalate oxygen atoms occupying one basal and one axial site), and trigonal bipyramidal in the zinc compound (III) (oxalate oxygens occupying one apical and one equatorial site). The conformations of the co-ordinated amines are discussed and their relationships with the stereochemistry of the metal centres and with the hydrogen bonding network examined.

Crystal data: (I), monoclinic *a* = 6·33(2), *b* = 12·03(2), *c* = 14·95(3) Å, β = 91·2(3)°, *Z* = 2, space group $P2_1/n$; (II), orthorhombic, *a* = 7·02(1), *b* = 13·25(3), *c* = 25·27(4) Å, *Z* = 4, space group $Pbc2_1$; (III), orthorhombic, *a* = 13·38(2), *b* = 14·72(3), *c* = 13·30(3) Å, *Z* = 4, space group $Pna2_1$. The structures were solved by the heavy-atom method from photographic data and refined by least squares to *R* 0·105 [(I), 1936 independent reflexions], 0·101 [(II), 1948], and 0·090 [(III), 1688].

THE preparations of several oxalato-amine derivatives of nickel(II), copper(II), and zinc(II) with a stoicheiometry featuring one oxalate to two metal ions have been reported.[1,2] As a consequence of their properties, particularly their i.r. absorptions, the compounds were assigned dimeric structures with the oxalate ion functioning as a planar bridging group through the formation of five-membered chelate rings with each of two metal ions. In choosing three of these complexes, $[\{Ni(en)_2\}_2(C_2O_4)](NO_3)_2$ (I), $[\{Cu(dien)\}_2(C_2O_4)](ClO_4)_2$ † (II), and $[\{Zn(dpt)\}_2(C_2O_4)](ClO_4)_2$ ‡ (III), for an *X*-ray crystallographic study of the role of the oxalate ion under what

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† dien = Di-(2-aminoethyl)amine, $\{NH_2\cdot[CH_2]_2\cdot\}_2NH$.

‡ dpt = Di-(3-aminopropyl)amine, $\{NH_2\cdot[CH_2]_3\cdot\}_2NH$.

[1] N. F. Curtis, *J. Chem. Soc.*, **1963**, 4109.

[2] N. F. Curtis, *J. Chem. Soc.* (*A*), **1968**, 1584.

was expected to be differing stereochemical situations, an examination of amine conformation was also contemplated.

The metal ions, high-spin d^8 nickel(II), d^9 copper(II), and d^{10} zinc(II), show progressively more variable co-ordination geometry. Compounds of nickel(II) are usually six-co-ordinate and octahedral unless the ligands have demanding steric requirements. Those of copper(II) show a greater variety of stereochemistries but with tetragonal structures (square planar, square pyramidal, and distorted octahedral) most common. The co-ordination arrangement about zinc(II) is largely determined by inter- and intra-ligand interactions and a variety of geometries have been observed. The series of dimeric amine–oxalate compounds which include (I), (II), and (III) illustrate these effects. With nickel(II) compounds are all six-co-ordinate, attempts to prepare triamine analogues of (II) or (III) yielding aquo-complexes $[\{Ni(N_3)(H_2O)\}_2(C_2O_4)]X_2$.[2] Copper(II) forms the bridging oxalato-compounds only with the triamines dien and dpt whereas zinc(II) complexes can be prepared with a number of amines. These are six-co-ordinate and isomorphous with their nickel(II) analogues when diamines, *e.g.* $[\{Zn(en)_2\}_2(C_2O_4)]_2$, or tetramines, $[\{Zn(trien)\}_2C_2O_4)]_2$, are employed,[2] but with the triamine dpt the five-co-ordinate compound (III), not isomorphous with its copper(II) analogue, was prepared.

The amines en, dien, and dpt have their own stereochemical properties which together with the co-ordination ' preferences ' of the metal ion and any other inter- or intra-molecular interactions determine the exact geometry of the structures adopted. For en these are simple and *gauche* conformations are observed.[3] Details and, where applicable, chirality, are determined largely by hydrogen bonding to the amino-groups, non-bonded interactions involving methylene groups and, for copper(II), by what appears to be an electronic effect which imposes asymmetry.[4] For the triamines, dien and dpt, two modes of co-ordination are possible, distinguished for an octahedral metal centre as facial (vicinal) or meridional (equatorial). Related configurations are possible for other co-ordination geometries. The relative stabilities of these two arrangements depend, among other things, on the metal–nitrogen distances, and vicinal co-ordination is observed in MoO_3(dien) [5] and $Mo(CO)_3$(dien) [6] where the metal–nitrogen distances are long. Meridional bonding is seen in $Ni(dien)_2Br_2,H_2O$,[7] $Cu(dien)_2,H_2O$,[8] $Cu(dien)_2(NO_3)_2$,[9] $Cu(dien)(C_2O_4),4H_2O$,[10] and $[Cu(dien)(HCO_2)](HCO_2)$.[11] The dpt compounds $[\alpha\text{-}Co(dpt)(en)Cl]I_2,H_2O$,[12] $[\beta\text{-}Co(dpt)(en)Cl]ZnCl_4$,[13] $[Ni(dpt)_2](ClO_4)_2$,[14] and $[Cu(dpt)(OAc)]ClO_4$ [15] also have the meridional arrangement. For dpt two conformations are apparent: either both chelate rings have a chair conformation as in $[Ni(dpt)_2](ClO_4)_2$, or they have chair–distorted boat conformations as in the Co^{II} and Cu^{II} examples. In the aforementioned dien compounds the chelate rings are all reported to have the *gauche* conformation, often very asymmetric. Metal–nitrogen bond lengths and chelate (NMN) bond-angle rigidity appear to be important factors in determining the conformations adopted, although in view of the limited number of reported structures the significance of hydrogen bonding and non-bonded interactions is not clear.

EXPERIMENTAL

Crystallographic Data.—(I). $C_{10}H_{32}N_{10}Ni_2O_{10}$, $M = 569{\cdot}8$, Monoclinic, $a = 6{\cdot}33(2)$, $b = 12{\cdot}03(2)$, $c = 14{\cdot}95(3)$ Å, $\beta = 91{\cdot}2(3)°$ (standard deviations from the spread of film measurements), $Z = 2$, $D_m = 1{\cdot}640(8)$ (inferring $Z = 1{\cdot}97$). Space group $P2_1/n$. 2226 Independent reflexions collected (290 unobserved) for layers 0—4*kl* and *h*0—8*l*. Crystal dimensions: $0{\cdot}30 \times 0{\cdot}15 \times 0{\cdot}14$ mm. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; $\mu(\text{Cu-}K_\alpha) = 27{\cdot}9\ cm^{-1}$.

(II). $C_{10}H_{26}Cl_2Cu_2N_6O_{12}$, $M = 620{\cdot}3$, Orthorhombic, $a = 7{\cdot}02(1)$, $b = 13{\cdot}25(3)$, $c = 25{\cdot}27(4)$ Å (standard deviations from spread of measurement), $Z = 4$, $D_m = 1{\cdot}812(7)$ (inferring $Z = 4{\cdot}02$). Space group $Pbc2_1$. 2400 (452 Unobserved) reflexions were collected for layers 0—5*kl* and *h*0—9*l*. Crystal dimensions: $0{\cdot}26 \times 0{\cdot}12 \times 0{\cdot}15$ mm. $\mu(\text{Cu-}K_\alpha) = 50{\cdot}6\ cm^{-1}$.

(III). $C_{14}H_{34}Cl_2N_6O_{12}Zn_2$, $M = 680{\cdot}1$, Orthorhombic, $a = 13{\cdot}38(2)$, $b = 14{\cdot}82(3)$, $c = 13{\cdot}30(3)$ Å (standard deviations from spread of measurements), $Z = 4$, $D_m = 1{\cdot}690(5)$ (inferring $Z = 3{\cdot}97$). Space group $Pna2_1$. 1915 (227 Unobserved) reflexions collected for layers 0—9*kl* and *hk*0—8. A separate needle-shaped crystal of hexagonal cross-section was used for each layer. Dimensions parallel to the needle (*a* axis) 0·42 and 0·21 mm, across a diagonal (*c* axis) 0·19 and 0·10 mm. $\mu(\text{Cu-}K_\alpha) = 47{\cdot}6\ cm^{-1}$.

Intensity data were collected by Weissenberg photographic methods and absorption corrections [16] applied to the sets from (II) and (III). Structure solutions were by conventional heavy-atom methods, the choice of non-centrosymmetric space group for (II) being dictated by the course of the refinement, that for (III) being implied by the Patterson function. Block-diagonal least-squares methods were used to adjust parameters with recourse to difference syntheses for (II) when progress was impeded by false symmetry. Standard scattering factors [17] were used, real dispersion corrections of $-3{\cdot}1$, $-2{\cdot}1$, and $-1{\cdot}7$ e being applied to nickel(0), copper(0), and zinc(0) values. The models adopted excluded hydrogen atoms until the last stages of refinement but progressively allowed for heavy-atom and then light-atom thermal anisotropy. Hydrogen atoms were finally placed at computed positions and their presence

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TABLE 1

Atom positions

(*a*) Compound (I)

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Ni	0·2547(2)	0·1547(1)	0·0780(1)
O(1)	0·1654(12)	0·0718(6)	0·8031(4)
O(2)	0·1389(17)	0·0741(8)	0·6609(5)
O(3)	0·3774(13)	0·1677(6)	0·7309(7)
O(4)	0·2519(7)	−0·0154(4)	0·0469(3)
O(5)	−0·0462(7)	0·1403(4)	0·0183(3)
N(1)	0·2294(10)	0·1051(5)	0·7294(4)
N(2)	0·1347(9)	0·1213(5)	0·2057(4)
N(3)	0·5440(10)	0·1407(5)	0·1474(4)
N(4)	0·3986(9)	0·1933(5)	−0·0425(4)
N(5)	0·2187(10)	0·3269(5)	0·0875(4)
C(1)	0·3083(15)	0·0788(8)	0·2614(5)
C(2)	0·5042(13)	0·1414(8)	0·2430(5)
C(3)	0·4298(13)	0·3140(7)	−0·0466(5)
C(4)	0·2405(15)	0·3712(6)	−0·0043(5)
C(5)	−0·0855(9)	0·0452(5)	−0·0093(4)
H(1,N2)	0·023	0·061	0·211
H(2,N2)	0·079	0·187	0·242
H(1,N3)	0·628	0·069	0·139
H(2,N3)	0·650	0·203	0·140
H(1,N4)	0·316	0·177	−0·099
H(2,N4)	0·546	0·163	−0·053
H(1,N5)	0·077	0·356	0·108
H(2,N5)	0·328	0·369	0·123
H(1,C1)	0·334	−0·009	0·246
H(2,C1)	0·266	0·088	0·332
H(1,C2)	0·637	0·102	0·278
H(2,C2)	0·478	0·227	0·266
H(1,C3)	0·446	0·339	−0·117
H(2,C3)	0·574	0·335	−0·010
H(1,C4)	0·097	0·353	−0·042
H(2,C4)	0·265	0·461	−0·001

(*b*) Compound (II)

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Cu(1)	0·2282(3)	0·1013(1)	0·0707
Cu(2)	−0·2297(3)	−0·0994(2)	−0·0704(1)
Cl(1)	0·3880(4)	−0·2510(4)	0·0026(2)
Cl(2)	−0·0586(6)	−0·0077(3)	0·2477(3)
O(1)	0·2602(17)	−0·3373(9)	0·0016(6)
O(2)	0·2842(20)	−0·1600(9)	−0·0017(8)
O(3)	0·4832(25)	−0·2419(14)	0·0474(5)
O(4)	0·5169(19)	−0·2541(10)	−0·0468(6)
O(5)	−0·0953(41)	0·0842(13)	0·2255(11)
O(6)	0·1173(40)	−0·0429(22)	0·2308(14)
O(7)	−0·2189(34)	−0·0724(18)	0·2418(12)
O(8)	−0·0499(32)	0·0032(18)	0·3022(6)
O(9)	−0·0281(15)	−0·0050(8)	0·0680(4)
O(10)	0·1847(15)	0·0857(8)	−0·0081(4)
O(11)	0·0110(16)	0·0108(8)	−0·0702(4)
O(12)	−0·1985(14)	−0·0798(7)	0·0062(4)
N(1)	0·4356(20)	−0·0075(10)	0·0793(6)
N(2)	0·2716(25)	0·1217(11)	0·1510(5)
N(3)	0·0926(17)	0·2231(9)	0·0750(5)
N(4)	−0·4648(15)	−0·0110(7)	−0·0735(5)
N(5)	−0·2735(16)	−0·1200(9)	−0·1466(5)
N(6)	−0·0632(17)	−0·2307(8)	−0·0772(6)
C(1)	0·4910(24)	−0·0168(11)	0·1310(5)
C(2)	0·4554(32)	0·0747(18)	0·1611(7)
C(3)	0·2418(30)	0·2291(14)	0·1577(6)
C(4)	0·0395(22)	0·2473(11)	0·1319(6)
C(5)	0·5214(41)	0·0077(20)	−0·1298(15)
C(6)	−0·4756(31)	−0·0842(16)	−0·1589(7)
C(7)	−0·2277(33)	−0·2251(13)	−0·1665(7)
C(8)	−0·0608(33)	−0·2671(14)	−0·1295(8)
C(9)	−0·0611(20)	−0·0252(10)	0·0191(5)
C(10)	0·0593(19)	0·0277(9)	−0·0232(5)
H(1,N1)	0·400	−0·080	0·071
H(2,N1)	0·563	0·005	0·062
H(1,N2)	0·175	0·086	0·174
H(1,N3)	0·166	0·284	0·062
H(2,N3)	−0·032	0·223	0·055
H(1,N4)	−0·584	−0·042	0·058

TABLE 1 (*Continued*)

(*b*) Compound (II)

Atom	*x*/*a*	*y*/*b*	*z*/*c*
H(2,N4)	−0·451	0·057	−0·056
H(1,N5)	−0·184	−0·070	−0·164
H(1,N6)	−0·107	−0·293	−0·057
H(2,N6)	0·078	−0·225	−0·070
H(1,C1)	0·412	−0·080	0·148
H(2,C1)	0·643	−0·034	0·131
H(1,C2)	0·567	0·129	0·151
H(2,C2)	0·463	0·056	0·203
H(1,C3)	0·355	0·270	0·137
H(2,C3)	0·245	0·248	0·200
H(1,C4)	−0·010	0·325	0·136
H(2,C4)	−0·069	0·196	0·147
H(1,C5)	−0·409	0·063	−0·153
H(2,C5)	−0·650	0·042	−0·141
H(1,C6)	−0·521	−0·095	−0·203
H(2,C6)	−0·592	−0·149	−0·141
H(1,C7)	−0·182	−0·221	−0·208
H(2,C7)	−0·355	−0·272	−0·164
H(1,C8)	0·079	−0·246	−0·145
H(2,C8)	−0·069	−0·349	−0·126

(*c*) Compound (III)

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Zn(1)	0·1012(2)	0·1341(1)	0·2500
Zn(2)	−0·0691(2)	0·3534(1)	−0·0355(2)
Cl(1)	0·2590(4)	0·4249(3)	0·0819(4)
Cl(2)	0·2590(4)	−0·0704(4)	0·1384(6)
O(1)	0·2326(23)	0·4636(23)	−0·0100(29)
O(2)	0·1876(22)	0·3646(20)	0·1072(32)
O(3)	0·2936(39)	0·4831(38)	0·1537(31)
O(4)	0·3431(21)	0·3772(26)	0·0696(25)
O(5)	0·1713(14)	−0·1157(13)	0·1261(20)
O(6)	0·3415(13)	−0·1219(12)	0·1457(24)
O(7)	0·2724(21)	0·0026(18)	0·0751(29)
O(8)	0·2503(29)	−0·0270(32)	0·2299(28)
O(9)	0·1039(9)	0·1580(8)	0·0865(9)
O(10)	0·0017(9)	0·2368(7)	0·2418(9)
O(11)	−0·0771(11)	0·3250(8)	0·1289(8)
O(12)	0·0221(9)	0·2463(8)	−0·0209(7)
N(1)	0·0211(11)	0·0174(12)	0·2245(12)
N(2)	0·1066(16)	0·1079(13)	0·4098(14)
N(3)	0·2402(13)	0·1912(16)	0·2491(17)
N(4)	−0·2195(13)	0·3280(15)	−0·0524(13)
N(5)	−0·0351(13)	0·3742(12)	−0·1912(12)
N(6)	−0·0167(13)	0·4771(12)	0·0093(13)
C(1)	−0·0427(28)	−0·0073(31)	0·3060(30)
C(2)	−0·0210(25)	−0·0060(18)	0·3954(21)
C(3)	0·0053(18)	0·0773(19)	0·4476(17)
C(4)	0·1425(24)	0·1876(18)	0·4673(16)
C(5)	0·2524(25)	0·2068(19)	0·4376(15)
C(6)	0·2650(20)	0·2515(17)	0·3343(15)
C(7)	−0·2417(21)	0·2775(18)	−0·1487(18)
C(8)	−0·2056(17)	0·3225(17)	−0·2408(18)
C(9)	−0·0929(23)	0·3113(17)	−0·2610(19)
C(10)	−0·0392(20)	0·4687(12)	−0·2305(14)
C(11)	0·0257(22)	0·5266(16)	−0·1624(21)
C(12)	−0·0150(18)	0·5512(15)	−0·0647(20)
C(13)	0·0399(12)	0·2184(10)	0·0615(12)
C(14)	−0·0152(12)	0·2664(11)	0·1511(12)
H(1,N1)	0·061	−0·041	0·215
H(2,N1)	−0·029	0·019	0·167
H(1,N2)	0·157	0·057	0·415
H(1,N3)	0·255	0·233	0·190
H(2,N3)	0·298	0·147	0·252
H(1,N4)	−0·264	0·383	−0·058
H(2,N4)	−0·251	0·288	0·000
H(1,N5)	0·037	0·354	−0·185
H(1,N6)	0·056	0·479	0·031
H(2,N6)	−0·056	0·508	0·064
H(1,C1)	−0·109	0·037	0·306
H(2,C1)	−0·066	−0·078	0·297
H(1,C2)	−0·087	−0·037	0·429
H(2,C2)	0·041	−0·054	0·397
H(1,C3)	−0·052	0·129	0·431
H(2,C3)	0·008	0·064	0·528

TABLE 1 (*Continued*)

(*c*) Compound (III)

Atom	*x*/*a*	*y*/*b*	*z*/*c*
H(1,C4)	0·095	0·246	0·449
H(2,C4)	0·137	0·173	0·547
H(1,C5)	0·285	0·252	0·493
H(2,C5)	0·293	0·142	0·436
H(1,C6)	0·216	0·311	0·329
H(2,C6)	0·343	0·273	0·325
H(1,C7)	−0·323	0·270	−0·156
H(2,C7)	−0·207	0·211	−0·146
H(1,C8)	−0·223	0·395	−0·234
H(2,C8)	−0·248	0·294	−0·304
H(1,C9)	−0·076	0·329	−0·340
H(2,C9)	−0·071	0·241	−0·247
H(1,C10)	−0·116	0·493	−0·230
H(2,C10)	−0·011	0·470	−0·308
H(1,C11)	0·042	0·590	−0·202
H(2,C11)	0·095	0·490	−0·148
H(1,C12)	−0·092	0·575	−0·076
H(2,C12)	0·031	0·606	−0·035

TABLE 2

Anisotropic thermal parameters [a]

(*a*) Compound (I)

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ni	76(2)	20(1)	12(1)	−14(2)	23(1)	−6(1)
O(1)	401(20)	85(5)	33(3)	−179(16)	85(12)	−2(6)
O(2)	760(36)	126(7)	37(3)	284(26)	−165(71)	49(8)
O(3)	377(20)	65(5)	105(5)	−135(17)	224(16)	−15(9)
O(4)	99(10)	20(3)	26(2)	8(9)	10(7)	−20(4)
O(5)	130(11)	24(3)	28(2)	5(9)	6(8)	−15(4)
N(1)	212(16)	40(4)	21(2)	42(14)	34(10)	−1(5)
N(2)	104(11)	41(4)	19(2)	0(12)	47(9)	18(5)
N(3)	147(14)	49(4)	23(2)	−20(13)	36(10)	−6(5)
N(4)	147(13)	46(4)	15(2)	5(13)	39(9)	−1(5)
N(5)	198(15)	27(3)	21(2)	−6(12)	70(9)	−6(5)
C(1)	240(21)	84(7)	22(3)	3(21)	7(13)	37(7)
C(2)	162(18)	91(7)	22(3)	−2(19)	7(12)	16(8)
C(3)	237(19)	49(5)	26(3)	−45(17)	73(12)	18(6)
C(4)	326(24)	27(4)	32(3)	31(17)	54(15)	12(6)
C(5)	59(11)	29(4)	17(2)	5(12)	25(8)	−6(5)

(*b*) Compound (II)

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Cu(1)	98(4)	18(1)	7(1)	−4(3)	−11(2)	−2(1)
Cu(2)	103(4)	19(1)	6(1)	−13(3)	−3(2)	−1(1)
Cl(1)	108(4)	16(1)	11(1)	−44(8)	−33(4)	3(1)
Cl(2)	253(8)	49(2)	8(1)	−43(7)	−0(7)	6(4)
O(1)	169(23)	42(6)	25(3)	−125(20)	78(13)	−48(7)
O(2)	185(26)	18(6)	40(4)	99(21)	50(19)	25(9)
O(3)	580(38)	82(11)	24(2)	−13(35)	−116(11)	−21(7)
O(4)	137(23)	47(7)	27(3)	31(24)	38(15)	56(7)
O(5)	618(92)	68(8)	77(7)	19(49)	−42(40)	136(10)
O(6)	667(75)	185(22)	64(10)	436(61)	209(40)	80(23)
O(7)	716(60)	172(15)	55(5)	−350(41)	−168(26)	−100(13)
O(8)	739(55)	244(18)	5(2)	−680(41)	−1(19)	−23(10)
O(9)	118(20)	30(6)	5(1)	−31(18)	−14(10)	1(5)
O(10)	111(18)	30(5)	4(1)	−57(17)	−5(9)	−2(5)
O(11)	143(19)	27(5)	6(1)	−76(17)	−14(10)	4(5)
O(12)	97(17)	17(4)	7(1)	−27(16)	9(9)	1(5)
N(1)	141(25)	30(7)	9(2)	−80(23)	25(12)	5(6)
N(2)	380(40)	30(7)	3(1)	−29(29)	−37(12)	−6(5)
N(3)	103(21)	23(6)	4(1)	−49(20)	−4(10)	1(5)
N(4)	56(18)	4(4)	10(2)	14(16)	3(10)	5(5)
N(5)	85(21)	19(5)	8(2)	63(18)	37(10)	6(5)
N(6)	131(20)	25(5)	15(2)	82(16)	2(13)	−1(7)
C(1)	190(30)	38(8)	3(2)	67(24)	−8(13)	7(6)
C(2)	276(46)	69(13)	9(3)	58(44)	−44(18)	−12(10)
C(3)	282(47)	43(10)	2(2)	−24(36)	−11(17)	−4(7)
C(4)	146(28)	17(6)	8(2)	57(25)	24(17)	10(7)
C(5)	266(57)	55(14)	42(7)	−32(49)	−94(34)	−9(19)
C(6)	220(41)	55(12)	12(3)	21(39)	−72(17)	−9(10)
C(7)	306(50)	26(8)	10(2)	22(35)	16(20)	−20(7)
C(8)	272(47)	35(9)	12(3)	−47(36)	43(20)	−6(9)
C(9)	100(25)	18(6)	4(2)	−31(22)	12(12)	−0(6)
C(10)	90(23)	8(5)	4(2)	21(20)	−24(10)	2(5)

TABLE 2 (*Continued*)

(*c*) Compound (III)

Atom	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Zn(1)	50(1)	34(1)	40(1)	0(2)	1(2)	19(2)
Zn(2)	53(1)	34(1)	39(1)	8(2)	−1(3)	16(2)
Cl(1)	53(3)	43(2)	89(4)	11(4)	−23(6)	1(5)
Cl(2)	61(3)	66(3)	124(5)	−23(5)	48(7)	7(7)
O(1)	158(23)	251(20)	463(33)	−68(36)	−253(43)	529(33)
O(2)	161(19)	210(19)	369(39)	−223(28)	−242(48)	365(42)
O(3)	323(48)	257(29)	290(30)	85(70)	−188(65)	−384(40)
O(4)	168(20)	320(31)	148(27)	274(36)	−52(41)	−42(54)
O(5)	80(11)	87(11)	167(20)	−44(18)	9(27)	−26(27)
O(6)	55(10)	67(9)	254(30)	8(16)	22(30)	50(29)
O(7)	164(22)	124(15)	356(34)	47(31)	161(49)	281(31)
O(8)	259(41)	301(39)	152(25)	139(62)	9(55)	−181(55)
O(9)	49(7)	46(6)	44(6)	25(11)	1(12)	11(11)
O(10)	65(8)	40(5)	32(6)	8(11)	−5(13)	21(11)
O(11)	90(10)	36(5)	32(6)	21(13)	−3(13)	19(10)
O(12)	68(8)	44(5)	17(5)	15(11)	−7(12)	8(10)
N(1)	49(10)	67(9)	58(10)	9(16)	−31(17)	8(17)
N(2)	111(15)	72(10)	50(9)	−45(22)	−15(22)	41(17)
N(3)	53(10)	112(14)	72(11)	18(21)	−3(24)	−48(25)
N(4)	59(10)	97(13)	58(11)	−8(20)	20(19)	−4(21)
N(5)	69(10)	64(9)	49(8)	20(17)	57(17)	35(15)
N(6)	69(11)	63(9)	55(9)	−17(18)	32(18)	−48(15)
C(1)	151(24)	206(30)	124(28)	−209(40)	28(37)	−46(53)
C(2)	205(26)	112(13)	90(16)	−216(27)	−56(36)	119(23)
C(3)	73(14)	114(17)	73(14)	−15(27)	54(24)	81(25)
C(4)	168(25)	93(14)	21(8)	−20(34)	−0(29)	−49(22)
C(5)	173(26)	84(15)	43(11)	−15(34)	−69(27)	−46(20)
C(6)	105(19)	67(11)	56(12)	−27(24)	15(28)	−33(21)
C(7)	114(19)	74(13)	57(12)	28(27)	−5(29)	44(23)
C(8)	70(13)	82(13)	60(12)	5(23)	−41(26)	8(24)
C(9)	151(23)	67(12)	56(13)	−27(31)	−6(32)	3(26)
C(10)	127(18)	36(7)	47(10)	−22(21)	−6(24)	56(14)
C(11)	108(20)	76(12)	131(18)	−23(26)	−3(35)	157(21)
C(12)	73(15)	55(10)	102(19)	−16(21)	7(29)	10(24)
C(13)	39(8)	25(6)	53(9)	−26(13)	60(16)	7(13)
C(14)	33(9)	39(8)	42(8)	−20(14)	8(16)	27(14)

[a] The scattering factor for an atom is expressed as:

$$f = f_o \exp - (b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl).$$

verified by difference-Fourier syntheses before their inclusion with temperature factors of 5·0 Å.[2] Further least-squares cycles were then computed, but the hydrogen parameters were not adjusted except to maintain their proper geometric relationships with other atoms. A weighting scheme of the form $w = [1 + (F_o - b)^2/a^2]^{-1}$ was used throughout, the parameters a and b being varied at intervals to keep $\langle w\Delta^2 \rangle$ constant over $|F_o|$ ranges. As the models were progressively made more complex, significance tests were applied to justify each alteration.[18] Final R values were 0·105 (I), 0·101 (II), and 0·090 (III).

Atomic co-ordinates and standard deviations are listed in Table 1, thermal parameters in Table 2, and calculated bond lengths and angles in Tables 3 and 4. The relevant atom numbering systems are shown in the Figure. Observed and calculated structure factors for each analysis are listed in Supplementary Publication No. SUP 20677 (8 pp., 1 microfiche).*

The standard deviations quoted in Tables 1—4 are those obtained from the least-squares variances and are expected to be under-estimated. A check of internal consistency between bonds of known equality, for use as a guide, is unfortunately not possible but experience suggests that actual values will be *ca.* 1·3—1·5 times those listed.

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue (items less than 10 pp. are supplied as full size copies).

[18] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

Table 3

Bond lengths (Å)

(*a*) Compound (I)

Nickel octahedron

Ni–N(2)	2·108(6)
Ni–N(3)	2·092(6)
Ni–N(4)	2·089(6)
Ni–N(5)	2·089(6)
Ni–O(4)	2·097(4)
Ni–O(5)	2·093(5)

Oxalate bridge

C(5)–C(5′) *	1·554(8)
C(5)–O(5)	1·239(7)
C(5′)–O(4)	1·236(7)

Ethylenediamine groups

N(2)–C(1)	1·457(10)
C(1)–C(2)	1·480(12)
C(2)–N(3)	1·458(11)
N(4)–C(3)	1·467(10)
C(3)–C(4)	1·529(11)
C(4)–N(5)	1·481(10)

Nitrate group

N(1)–O(1)	1·248(9)
N(1)–O(2)	1·221(11)
N(1)–O(3)	1·201(10)

(*b*) Compound (II)

Copper square pyramids

Cu(1)–N(1)	2·06(1)
Cu(1)–N(2)	2·07(1)
Cu(1)–N(3)	1·88(1)
Cu(1)–O(9)	2·29(1)
Cu(1)–O(10)	2·02(1)
Cu(1)–O(3′)	2·96
Cu(2)–N(4)	2·02(1)
Cu(2)–N(5)	1·97(1)
Cu(2)–N(6)	2·10(1)
Cu(2)–O(11)	2·23(1)
Cu(2)–O(12)	1·97(1)
Cu(2)–O(4″)	2·78

Oxalate bridge

C(9)–C(9)	1·29(2)
C(9)–O(12)	1·25(2)
C(9)–C(10)	1·53(2)
C(10)–O(10)	1·23(2)
C(10)–O(11)	1·26(2)

Diethylenetriamine groups

N(1)–C(1)	1·37(2)
C(1)–C(2)	1·45(3)
C(2)–N(2)	1·45(3)
N(2)–C(3)	1·45(2)
C(3)–C(4)	1·58(3)
C(4)–N(3)	1·52(2)
N(4)–C(5)	1·50(3)
C(5)–C(6)	1·46(4)
C(6)–N(5)	1·53(3)
N(5)–C(7)	1·51(2)
C(7)–C(8)	1·60(3)
C(8)–N(6)	1·41(3)

Perchlorate anions

Cl(1)–O(1)	1·45(1)
Cl(1)–O(2)	1·41(1)
Cl(1)–O(3)	1·32(2)
Cl(1)–O(4)	1·54(2)
Cl(2)–O(5)	1·37(2)
Cl(2)–O(6)	1·39(3)
Cl(2)–O(7)	1·42(3)
Cl(2)–O(8)	1·39(2)

(*c*) Compound (III)

Zinc trigonal bipyramids

Zn(1)–N(1)	2·05(2)
Zn(1)–N(2)	2·16(2)
Zn(1)–N(3)	2·04(2)
Zn(1)–O(9)	2·20(1)
Zn(1)–O(10)	2·02(1)
Zn(1)–O(8)	3·11
Zn(2)–N(4)	2·06(2)
Zn(2)–N(5)	2·14(2)
Zn(2)–N(6)	2·04(2)
Zn(2)–O(11)	2·23(1)
Zn(2)–O(12)	2·00(1)

Oxalate bridge

C(13)–C(14)	1·57(2)
C(13)–O(9)	1·28(2)
C(13)–O(12)	1·19(2)
C(14)–O(10)	1·30(2)
C(14)–O(11)	1·23(2)

Dipropylenetriamine groups

N(1)–C(1)	1·43(4)
C(1)–C(2)	1·23(5)
C(2)–C(3)	1·45(4)
C(3)–N(2)	1·52(3)
N(2)–C(4)	1·48(3)
C(4)–C(5)	1·55(5)
C(5)–C(6)	1·53(3)
C(6)–N(3)	1·48(3)
N(4)–C(7)	1·51(3)
C(7)–C(8)	1·47(4)
C(8)–C(9)	1·54(4)
C(9)–N(5)	1·52(3)
N(5)–C(10)	1·49(3)
C(10)–C(11)	1·52(4)
C(11)–C(12)	1·45(4)
C(12)–N(6)	1·47(3)

Perchlorate anions

Cl(1)–O(1)	1·39(5)
Cl(1)–O(2)	1·35(4)
Cl(1)–O(3)	1·36(5)
Cl(1)–O(4)	1·34(4)
Cl(2)–O(5)	1·36(2)
Cl(2)–O(6)	1·34(2)
Cl(2)–O(7)	1·38(4)
Cl(2)–O(8)	1·38(4)

* C(5′) is related to C(5) by a centre at 0,0,0.

Table 4

Bond angles (°)

(*a*) Compound (I)

Nickel octahedron

N(2)–Ni–N(3)	82·2(5)
N(2)–Ni–N(4)	174·7(5)
N(2)–Ni–N(5)	94·9(5)
N(2)–Ni–O(4)	90·8(5)
N(2)–Ni–O(5)	91·7(5)
N(3)–Ni–N(4)	93·0(5)
N(3)–Ni–N(5)	98·2(5)
N(3)–Ni–O(4)	92·0(5)
N(3)–Ni–O(5)	169·6(5)
N(4)–Ni–N(5)	83·6(5)
N(4)–Ni–O(4)	91·6(5)
N(4)–Ni–O(5)	93·4(5)
N(5)–Ni–O(4)	169·0(5)
N(5)–Ni–O(5)	90·6(5)
O(4)–Ni–O(5)	79·7(4)

Oxalate bridge

Ni–O(5)–C(5)	113·1(6)
Ni–O(4)–C(5′)	112·7(6)
O(5)–C(5)–O(4′)	125·6(6)
O(5)–C(5)–C(5′)	116·8(7)
C(5)–C(5′)–O(4)	117·5(7)

Ethylenediamine groups

Ni–N(2)–C(1)	107·6(7)
N(2)–C(1)–C(2)	109·9(9)
C(1)–C(2)–N(3)	110·0(9)
C(2)–N(3)–Ni	108·6(7)
Ni–N(4)–C(3)	108·5(7)
N(4)–C(3)–C(4)	108·7(9)
C(3)–C(4)–N(5)	108·1(9)
C(4)–N(5)–Ni	106·3(8)

Nitrate anion

O(1)–N(1)–O(2)	119·2(11)
O(1)–N(1)–O(3)	116·8(10)
O(2)–N(1)–O(3)	124·0(11)

(*b*) Compound (II)

Copper square pyramids

N(1)–Cu(1)–N(2)	83·3(8)
N(1)–Cu(1)–N(3)	162·5(7)
N(1)–Cu(1)–O(9)	97·4(7)
N(1)–Cu(1)–O(10)	98·0(7)
N(2)–Cu(1)–N(3)	84·5(8)
N(2)–Cu(1)–O(9)	103·0(7)
N(2)–Cu(1)–O(10)	178·3(7)
N(3)–Cu(1)–O(9)	97·6(7)
N(3)–Cu(1)–O(10)	94·0(7)
O(9)–Cu(1)–O(10)	77·9(6)
N(1)–Cu(1)–O(3′)	92
N(2)–Cu(1)–O(3′)	90
N(3)–Cu(1)–O(3′)	76
O(9)–Cu(1)–O(3′)	165
O(10)–Cu(1)–O(3′)	89
Cu(1)–O(3′)–Cl(1′)	117
N(4)–Cu(2)–N(5)	85·1(7)
N(4)–Cu(2)–N(6)	158·1(7)
N(4)–Cu(2)–O(11)	103·9(7)
N(4)–Cu(2)–O(12)	93·0(7)
N(5)–Cu(2)–N(6)	83·8(7)
N(5)–Cu(2)–O(11)	102·2(7)
N(5)–Cu(2)–O(12)	117·4(7)
N(6)–Cu(2)–O(11)	96·9(7)
N(6)–Cu(2)–O(12)	97·3(7)
O(11)–Cu(2)–O(12)	80·0(6)
N(4)–Cu(2)–O(4″)	85
N(5)–Cu(2)–O(4″)	90
N(6)–Cu(2)–O(4″)	76
O(11)–Cu(2)–O(4″)	165
O(12)–Cu(2)–O(4″)	88
Cu(2)–O(4″)–Cl(1″)	122

Oxalate bridge

Cu(1)–O(9)–C(9)	107·3(9)
Cu(1)–O(10)–C(10)	118·5(9)
Cu(2)–O(11)–C(10)	108·9(9)
Cu(2)–O(12)–C(9)	114·8(9)
O(9)–C(9)–O(12)	120·6(11)
O(9)–C(9)–C(10)	118·4(11)
O(12)–C(9)–C(10)	120·7(11)
O(10)–C(10)–O(11)	126·8(11)
O(10)–C(10)–C(9)	117·7(11)
O(11)–C(10)–C(9)	115·4(11)

Diethylenetriamine groups

Cu(1)–N(1)–C(1)	111·4(10)
N(1)–C(1)–C(2)	112·2(12)
C(1)–C(2)–N(2)	114·7(13)
C(2)–N(2)–Cu(1)	104·3(11)
C(2)–N(2)–C(3)	121·9(12)
Cu(1)–N(2)–C(3)	102·7(11)
N(2)–C(3)–C(4)	103·4(12)
C(3)–C(4)–N(3)	97·9(11)
C(4)–N(3)–Cu(1)	111·2(9)
Cu(2)–N(4)–C(5)	110·4(12)
N(4)–C(5)–C(6)	106·4(15)
C(5)–C(6)–N(5)	111·1(14)
C(6)–N(5)–Cu(2)	107·6(10)
C(6)–N(5)–C(7)	114·5(12)
Cu(2)–N(5)–C(7)	114·8(10)
N(5)–C(7)–C(8)	106·4(12)
C(7)–C(8)–N(6)	114·9(13)
C(8)–N(6)–Cu(2)	111·5(11)

Perchlorate anions

O(1)–Cl(1)–O(2)	110·5(10)
O(1)–Cl(1)–O(3)	113·5(11)
O(1)–Cl(1)–O(4)	109·1(9)
O(2)–Cl(1)–O(3)	104·4(11)
O(2)–Cl(1)–O(4)	105·3(10)
O(3)–Cl(1)–O(4)	113·5(10)
O(5)–Cl(2)–O(6)	109·9(14)
O(5)–Cl(2)–O(7)	110·1(13)
O(5)–Cl(2)–O(8)	109·0(13)
O(6)–Cl(2)–O(7)	118·0(14)
O(6)–Cl(2)–O(8)	107·6(13)
O(7)–Cl(2)–O(8)	101·6(13)

(*c*) Compound (III)

Zinc trigonal bipyramids

N(1)–Zn(1)–N(2)	91·8(8)
N(1)–Zn(1)–N(3)	145·0(9)
N(1)–Zn(1)–O(9)	88·8(8)
N(1)–Zn(1)–O(10)	105·9(8)
N(2)–Zn(1)–N(3)	92·8(9)
N(2)–Zn(1)–O(9)	177·0(8)
N(2)–Zn(1)–O(10)	102·1(8)
N(3)–Zn(1)–O(9)	85·0(8)
N(3)–Zn(1)–O(10)	107·0(8)
O(9)–Zn(1)–O(10)	80·6(7)

TABLE 4 (*Continued*)

(*c*) Compound (III)

Zinc trigonal bipyramids	
N(4)–Zn(2)–N(5)	97·4(8)
N(4)–Zn(2)–N(6)	122·0(9)
N(4)–Zn(2)–O(11)	91·5(8)
N(4)–Zn(2)–O(12)	117·6(8)
N(5)–Zn(2)–N(6)	94·7(8)
N(5)–Zn(2)–O(11)	170·2(8)
N(5)–Zn(2)–O(12)	94·4(8)
N(6)–Zn(2)–O(11)	84·1(8)
N(6)–Zn(2)–O(12)	117·7(8)
O(11)–Zn(2)–O(12)	77·7(7)
N(1)–Zn(1)–O(8)	72
N(2)–Zn(1)–O(8)	86
N(3)–Zn(1)–O(8)	74
O(9)–Zn(1)–O(8)	92
O(10)–Zn(1)–O(8)	172
Zn(1)–O(8)–Cl(2)	119
Oxalate bridge	
Zn(1)–O(9)–C(13)	111·0(10)
Zn(1)–O(10)–C(14)	114·6(10)
Zn(2)–O(11)–C(14)	109·5(10)
Zn(2)–O(12)–C(13)	118·8(10)
O(9)–C(13)–O(12)	127·7(12)
O(9)–C(13)–C(14)	115·4(12)
O(12)–C(13)–C(14)	116·7(12)
O(10)–C(14)–O(11)	125·0(12)
O(10)–C(14)–C(13)	118·1(12)
O(11)–C(14)–C(13)	116·6(12)
Dipropylenetriamine groups	
Zn(1)–N(1)–C(1)	113·5(14)
N(1)–C(1)–C(2)	126·3(20)
C(1)–C(2)–C(3)	122·3(19)
C(2)–C(3)–N(2)	108·0(15)
C(3)–N(2)–Zn(1)	110·5(12)
C(3)–N(2)–C(4)	110·8(14)
Zn(1)–N(2)–C(4)	112·2(12)
N(2)–C(4)–C(5)	108·7(15)
C(4)–C(5)–C(6)	114·3(15)
C(5)–C(6)–N(3)	113·9(14)
C(6)–N(3)–Zn(1)	116·6(12)
Zn(2)–N(4)–C(7)	111·9(12)
N(4)–C(7)–C(8)	114·8(14)
C(7)–C(8)–C(9)	114·7(15)
C(8)–C(9)–N(5)	109·0(14)
C(9)–N(5)–Zn(2)	113·2(12)
C(9)–N(5)–C(10)	109·6(13)
Zn(2)–N(5)–C(10)	117·7(11)
N(5)–C(10)–C(11)	107·2(14)
C(10)–C(11)–C(12)	117·4(15)
C(11)–C(12)–N(6)	114·8(15)
C(12)–N(6)–Zn(2)	118·2(12)
Perchlorate anions	
O(1)–Cl(1)–O(2)	107·9(16)
O(1)–Cl(1)–O(3)	116·3(17)
O(1)–Cl(1)–O(4)	108·7(16)
O(2)–Cl(1)–O(3)	118·6(17)
O(2)–Cl(1)–O(4)	106·4(15)
O(3)–Cl(1)–O(4)	97·5(16)
O(5)–Cl(2)–O(6)	116·1(12)
O(5)–Cl(2)–O(7)	115·0(13)
O(5)–Cl(2)–O(8)	105·1(14)
O(6)–Cl(2)–O(7)	112·2(14)
O(6)–Cl(2)–O(8)	105·5(15)
O(7)–Cl(2)–O(8)	100·9(15)

DISCUSSION

ORTEP Diagrams of the three complex ions are shown in Figure 1. From these and the appropriate bond length and angle data it can be seen that the co-ordination stereochemistry about the metal ions is different for the three compounds, being essentially octahedral in (I), tetragonal pyramidal in (II), and trigonal bipyramidal in (III). Nevertheless each complex has a dimeric cation in which two metal atoms are symmetrically bridged by an oxalate group. The structures of the cations, the structures of the anions, and the hydrogen bonding and molecular packing are considered separately.

Structure of Cations.—(*a*) *The metal–oxalate groupings*. The oxalato-group is bichelate and bound in such a way as to complete a five-, rather than a four-membered ring, with each metal. Table 5 lists planes of best fit and the deviations therefrom of selected atoms. The oxalate ion has a similar structural role in $Fe(C_2O_4),2H_2O$,[19] $Ti(C_2O_4),10H_2O$,[20] $(NH_4)_2(VO_2)_2(C_2O_4)$,[21] β-$Cu(NH_3)_2(C_2O_4)$,[22] $Cu(NH_3)_3(C_2O_4)$,[23] and [Ru_2(pyridine)$_8C_2O_4$]$(BF_4)_2$.[24]

In all instances the bridging group is essentially planar,

TABLE 5

Planes of best fit and deviations therefrom. Equations are expressed in the cosine form $lX + mY + nZ + p = 0$, with reference to cell axes and with p expressed in Å units

(*a*) Compound (I)

(i) Definition of plane	l	m	n	p
(*a*): O(4), O(5), C(5), O(4′), O(5′), C(5′)	0·420	0·215	−0·882	0
(*b*): Ni, Ni′, O(4), O(4′), O(5), O(5′), C(5), C(5′)	0·414	0·208	−0·886	0
(*c*): N(1), O(1)—(3)	0·624	−0·780	−0·046	0·734
(*d*): Ni, O(4), O(5), N(3), N(5)	0·461	0·150	−0·874	0·016
(*e*): Ni, N(2), N(3)	0·022	−0·980	−0·197	2·018
(*f*): Ni, N(4), N(5)	0·876	0·065	0·478	−2·068

(ii) Deviations (Å) from planes

Plane (*a*):
O(4) 0·004, O(5) −0·004, C(5) −0·014, Ni 0·036, Ni′ −0·036, *etc.*

Plane (*b*):
Ni 0·009, O(4) −0·007, O(5) −0·015, C(5) 0·014, Ni′ −0·009, *etc.*, N(3) 0·197, N(5) −0·219

Plane (*c*):
N(1) 0·004, O(1) −0·001, O(2) −0·001, O(3) −0·001

Plane (*d*):
Ni 0·007, O(4) 0·103, O(5) −0·107, N(3) −0·090, N(5) 0·088, N(2) −2·091, N(4) 2·090

Plane (*e*):
C(1) 0·361, C(2) −0·296

Plane (*f*):
C(3) 0·239, C(4) −0·475

(*b*) Compound (II)

(i) Definition of plane	l	m	n	p
(*a*): O(9), O(10), O(11), O(12), C(9), C(10)	0·632	−0·775	0·003	0·049
(*b*): O(9)—(12)	0·632	−0·775	0·003	0·064
(*c*): N(1)–(3), O(10)	−0·771	−0·606	0·194	1·819
(*d*): N(4)—(6), O(12)	−0·702	−0·684	0·199	−1·867
(*e*): Cu(1), N(1), N(2)	−0·704	−0·682	0·197	1·692
(*f*): Cu(1), N(2), N(3)	−0·839	−0·508	0·194	1·680
(*g*): Cu(2), N(4), N(5)	−0·573	−0·794	0·204	−1·605
(*h*): Cu(2), N(5), N(6)	−0·802	−0·506	0·208	−1·661

(ii) Deviations (Å) from planes

Plane (*a*):
O(9) −0·020, O(10) −0·011, O(11) −0·018, O(12) −0·014, C(9) 0·037, C(10) 0·026, Cu(1) 0·027, Cu(2) 0·043, N(2) 0·016, N(5) 0·055

Plane (*b*):
O(9) −0·003, O(10) 0·003, O(11) −0·003, O(12) 0·003, C(9) 0·053, C(10) 0·041, Cu(1) 0·043, Cu(2) 0·060, N(2) 0·032, N(5) 0·071

Plane (*c*):
N(1) −0·094, N(2) 0·109, N(3) −1·106, O(12) 0·091, Cu(1) 0·115, O(9) 2·344

Plane (*d*):
N(4) 0·156, N(5) −0·167, N(6) 0·146, O(12) −0·135, Cu(2) −0·188, O(11) −2·372

Plane (*e*):
C(1) 0·066, C(2) −0·434, O(9) * +

Plane (*f*):
C(3) −0·515, C(4) 0·428, O(9) * +

Plane (*g*):
C(5) −0·260, C(6) 0·372, O(11) * −

Plane (*h*):
C(7) 0·416, C(8) −0·018, O(11) * −

* The sign of the displacements is given for the apical atoms.

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TABLE 5 (*Continued*)

(*c*) Compound (III)

(i) Definition of plane	*l*	*m*	*n*	*p*
(*a*): O(9)—(12), C(13), C(14)	0·722	0·687	0·080	−2·682
(*b*): Zn(1), N(1), N(3), O(10)	0·051	0·069	−0·996	2·982
(*c*): Zn(2), N(4), N(6), O(12)	0·179	0·142	−0·973	−0·892
(*d*): Zn(1), N(1), C(2), C(3)	−0·843	0·497	−0·205	0·791
(*e*): Zn(1), N(2), C(1), C(2)	0·699	−0·699	−0·153	0·940
(*f*): N(1), N(2), C(1), C(3)	0·495	−0·824	0·275	−0·826
(*g*): Zn(1), N(2), C(5), C(6)	0·644	−0·741	−0·194	1·267
(*h*): Zn(1), N(3), C(4), C(5)	0·344	−0·929	0·135	0·983
(*i*): N(2), N(3), C(4), C(6)	−0·742	0·588	−0·321	1·831
(*j*): Zn(2), N(4), C(8), C(9)	0·078	−0·988	0·132	5·196
(*k*): Zn(2), N(5), C(7), C(8)	0·429	−0·895	−0·118	4·924
(*l*): N(4), N(5), C(7), C(9)	−0·485	0·795	−0·365	−5·527
(*m*): Zn(2), N(5), C(11), C(12)	−0·930	0·268	−0·253	−2·453
(*n*): Zn(2), N(6), C(10) C(11)	−0·889	0·454	0·063	−3·258
(*o*): N(5), N(6), C(10), C(12)	−0·995	0·042	0·090	−0·495

(ii) Deviations (Å) from planes

Plane (*a*):
O(9) 0·011, O(10) −0·013, O(11) −0·003, O(12) 0, C(13) −0·022, C(14) 0·027, Zn(1) −0·083, Zn(2) 0·188, N(2) −0·126, N(5) 0·562

Plane (*b*):
Zn(1) −0·119, N(1) 0·045, N(3) 0·046, O(10) 0·027, O(9) 2·070, N(2) −2·262

Plane (*c*):
Zn(2) 0·146, N(4) −0·049, N(6) −0·049, O(12) −0·048, O(11) −2·061, N(5) 2·288

Plane (*d*):
Zn(1) −0·052, N(1) 0·069, C(2) −0·094, C(3) 0·076, N(2) −0·739, C(1) 0·386

Plane (*e*):
Zn(1) 0·002, N(2) −0·003, C(1) −0·004, C(2) 0·005, N(1) 0·504, C(3) −71·2

Plane (*f*):
N(1) −0·077, N(2) 0·069, C(1) 0·098, C(3) −0·091, Zn(1) −0·868, C(2) 0·555

Plane (*g*):
Zn(1) 0·036, N(2) −0·045, C(5) 0·060, C(6) −0·052, N(3) 0·611, C(4) −0·753

Plane (*h*):
Zn(1) 0·065, N(3) −0·080, C(4) −0·087, C(5) 0·102, N(2) 0·734, C(6) −0·637

Plane (*i*):
N(2) −0·041, N(3) 0·041, C(4) 0·048, C(6) −0·048, Zn(1) 0·921, C(5) −0·750

Plane (*j*):
Zn(2) −0·080, N(4) 0·102, C(8) −0·134, C(9) 0·111, N(5) −0·620, C(7) 0·644

Plane (*k*)
Zn(2) −0·074, N(5) 0·091, C(7) 0·112, C(8) −0·129, N(4) −0·577, C(9) 0·697

Plane (*l*)
N(4) −0·010, N(5) 0·010, C(7) 0·012, C(9) −0·012, Zn(2) −0·770, C(8) 0·751

Plane (*m*):
Zn(2) −0·080, N(5) 0·104, C(11) −0·148, C(12) 0·124, N(6) −0·395, C(10) 0·659

Plane (*n*):
Zn(2) −0·105, N(6) 0·138, C(10) 0·146, C(11) −0·180, N(5) −0·501, C(12) 0·550

Plane (*o*):
N(5) −0·029, N(6) 0·030, C(10) 0·036, C(12) −0·037, Zn(2) 0·589, C(11) −0·710

indisputably so in compounds (I) and (III) but with the likelihood that the carbon atoms in (II) are removed slightly [by 0·053(14) and 0·041(13) Å for C(9) and C(10) respectively, deviations being in the direction perpendicular to the plane] from the plane through the four oxalate oxygen atoms. In each compound the central bond of the oxalate group is 1·54 Å [1·554(8), 1·53(2), and 1·57(2) Å for the three complexes]. The mean carbon–oxygen lengths are *ca.* 1·25 Å in each compound, those in (I) and (II) probably being equal [1·239(7) and 1·236(7) Å in centrosymmetric (I), 1·23(2), 1·25(2), 1·26(2), and 1·29(2) Å in (II)] but those in (III) are divided into longer and shorter pairs [1·28(2), 1·30(2), and 1·19(2), 1·23(2) Å] although such a distinction is close to the limit of significance. The oxalate group in ionic compounds is found to be symmetrical with the C–O distance *ca.* 1·25 Å. For the acid dihydrate however, the C–OH and C=O distances are 1·281 and 1·207 Å respectively,[25] hydrogen bonding, or co-ordination of one oxygen of the carboxyl group,[10] partially localising the negative charge on the interacting atom with increase in that C–O distance and decrease in the other. Nevertheless the distance appears to be relatively insensitive to interactions by the oxygen atoms as can be seen from the lack of correlation between the C–O and M–O distances for (II) and (III). Thus the division of the C–O bonds in (III) into longer and shorter pairs is unlikely to reflect differences in donor bonding. On the other hand, the two zinc atoms have different co-ordination geometries, that at Zn(2) being close to trigonal bipyramidal with that at Zn(1) being describable in terms of a distorted octahedron if a perchlorate oxygen in the equatorial plane [Zn(1)–O(8) 3·11 Å] be assumed a member of the co-ordination sphere. It is perhaps significant therefore that the two long C–O bonds are associated with the same metal centre, Zn(1), the lengthening being assumed to be steric rather than electronic, in origin. The Cu–O(apical) distances in (II) are 2·23 and 2·29 Å appreciably longer than the Cu–O(basal) distances of 1·97 and 2·02 Å, as expected. In (III), the Zn–O(apical) distances of 2·20 and 2·23 Å. are again longer than the Zn–O(eq) distances of 2·00 and 2·02 Å.

In all compounds the oxalate groups span co-ordinating positions which would be ideally at 90° to one another, although in all instances this angle is reduced to *ca.* 80°. These are adjacent octahedral positions in (I), where the oxygen–metal–oxygen bond angle is 80°, basal and apical positions in (II) (78 and 80°) and apical and equatorial positions in (III) (78 and 81°). The dimensions of the oxalate ion are relatively insensitive to co-ordination and hence the angle subtended at a metal by an oxalato-group is largely determined by the M–O distances. Thus in $Zr(C_2O_4)_4,3H_2O$ [26] where Zr–O is *ca.* 2·2 Å this angle is 71·3°, whereas in $[Cr(en)_2(C_2O_4)][Cr(en)(C_2O_4)_2],2H_2O$ [27]

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with Cr–O *ca.* 1·95 Å it is 83°. (Similar values are seen in $K[Cr(C_2O_4)_2(H_2O)_2],3H_2O$.[28]) In (I), (II), and (III), and in $[Ru_2(pyridine)_8(C_2O_4)](BF_4)_2$,[24] the M–O distances are *ca.* 2·1 Å and the angle *ca.* 80°.

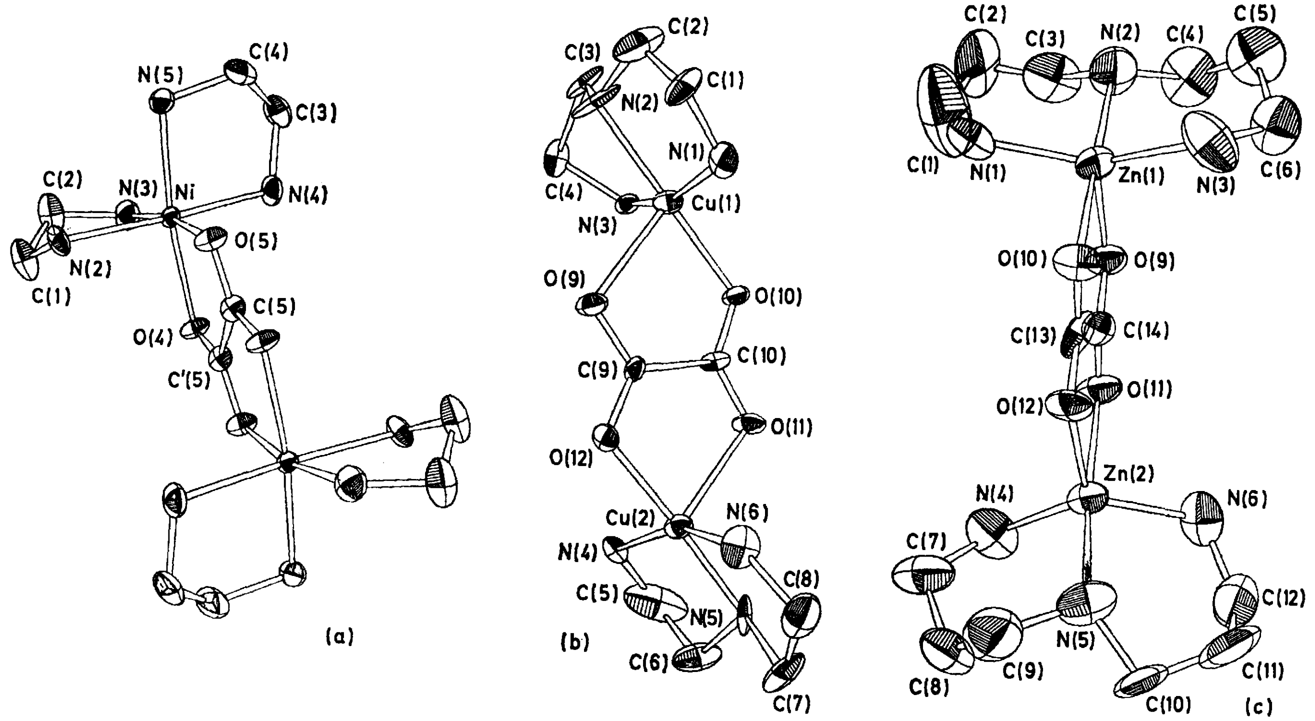

FIGURE 1 Thermal vibration ellipsoids of the complex cations, showing the atom numbering: (a) (I) $[\{Ni(en)_2\}_2(C_2O_4)]^{2+}$ [nitrate ion numbered as N(1), O(1)—(3)]; (b) (II) $[\{Cu(dien)\}_2(C_2O_4)]^{2+}$ [perchlorate ions numbered as Cl(1), O(1)—(4) and Cl(2), O(5)—(8)]; (c) (III) $[\{Zn(dpt)\}_2(C_2O_4)]^{2+}$ [perchlorate numbered as for (II)]

One unusual feature of the structure of (II) is the low value [121(1)°] found for one of the O–C–O angles which are normally close to 126° in other reported oxalate structures. Other values in the present structures are 125·6(6) in (I), 127(1) in (II), and 125(1) and 128(1)° in (III). The temptation to dismiss an aberrant value must be tempered by the knowledge that similar, but smaller, differences occur in the monomeric complex $Cu(dien)C_2O_4,4H_2O$,[10] for which more precise data are available. A comparison of copper–oxalate groupings (Table 6) between this complex and (II), which is essentially its dimeric analogue, shows that the dimensions of the oxalate differ little in the two modes of co-ordination although a C–O bond-length order O(basal) > O(apical) > O(non-bonded) is evident in the monomer.

Again, in all compounds, the metal atoms are found to be slightly but significantly out of planarity with the oxalato-bridging groups, the deviations (perpendicular to the planes) being: ±0·036(1) (I), 0·027(2) and 0·043(2) (II), and −0·083(3) and 0·188(3) Å (III). Whether this is a phenomenon to be regarded as a restricted version of the 'stepping' seen in some co-ordination compounds [29] or as the sort of distortion from simplistic expectations of linearity or coplanarity observed in transition-metal carbonyl and π-alkyl complexes [30,31] is not clear. The effect could equally result from packing requirements since the crystal structures of all the compounds involve hydrogen-bonding networks and close intermolecular contacts. The detailed study of the dimeric centrosymmetric molecule $[Ru_2(pyridine)_8(C_2O_4)](BF_4)_2$ reveals a geometry for the oxalate bridge closely parallel to that of compound (I), which suggests that the effects noted may be general.

TABLE 6

Oxalato-geometry in (*a*) $Cu(dien)C_2O_4,4H_2O$ and (*b*) (II)

Distances (Å)	(*a*)	(*b*)
Cu–O(bas)	1·965(6)	2·02, 1·97(1)
Cu–O(ap)	2·230(6)	2·29, 2·23(1)
C–O(bas)	1·275(10)	1·23, 1·25(2)
C–O(ap)	1·248(10)	1·29, 1·26(2)
C–C	1·560(11)	1·53(2)
C–O	1·227, 1·233(10)	
Angles (°)		
O(bas)–Cu–O(ap)	78·8(2)	77·9, 80·0(6)
Cu–O(bas)–C	117·7(5)	118·5, 114·8(9)
Cu–O(ap)–C	111·2(5)	107·3, 108·9(9)
O(bas)–C–C	117·1(7)	118, 121(1)
O(ap)–C–C	115·1(7)	118, 115(1)
O(bas)–C–O	123·4(8)	
O(ap)–C–O	128·7(8)	
O(bas)–C–O(ap)		121, 127(1)

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(*b*) *The metal–amine groupings.* (i) $[\{Ni(en)_2\}_2(C_2O_4)](NO_3)_2$, (I). The stereochemistry about the nickel ion resembles that [32] of $[Ni(en)_3]^{2+}$ with one en replaced by the bridging oxalato-group. Bond lengths and angles in the Ni(en) moieties accord with literature values and each have an asymmetrical *gauche* conformation [Tables 3(*a*) and 4(*a*); planes of Table 5 (I)]. Most en complexes of nickel(II) appear to have symmetrically staggered chelate rings but asymmetry is common with copper, for example. The extensive hydrogen-bonding network, involving the nitrogen donors (see later) may determine the details of the conformation. The two chelate rings at each metal centre have the δλ configurations.

TABLE 7

Intermolecular approaches (Å) less than the sum of van der Waals radii (taken as 1·6 for nitrogen and oxygen, 1·8 Å for carbon and chlorine)

(*a*) Compound (I)

O(1) $\cdots$ N($2'^{\mathrm{I}}$)	3·00	O(3) $\cdots$ N($5'^{\mathrm{V}}$)	3·08
O(1) $\cdots$ N($3'^{\mathrm{II}}$)	3·22	O(1) $\cdots$ C($5'^{\mathrm{III}}$)	3·27
O(1) $\cdots$ N($4'^{\mathrm{III}}$)	3·08	O(1) $\cdots$ C($5'^{\mathrm{I}}$)	3·44
O(2) $\cdots$ N($5'^{\mathrm{IV}}$)	3·09	O(4) $\cdots$ N($4'^{\mathrm{VI}}$)	3·08
O(3) $\cdots$ N($2'^{\mathrm{V}}$)	3·04		

Roman numerals as superscripts refer to the following transformations of the atoms, relative to the molecule at *x*, *y*, *z*

I $-x, -y, 1 - z$
II $1 - x, -y, 1 - z$
III $x, y, 1 + z$
IV $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$
V $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$
VI $1 - x, -y, -z$

(*b*) Compound (II)

C(8) $\cdots$ O($11'^{\mathrm{I}}$)	3·32	C(9) $\cdots$ O($2'$)	3·06
N(1) $\cdots$ O($12'^{\mathrm{II}}$)	3·31	C(10) $\cdots$ O($1'^{\mathrm{III}}$)	2·94
N(3) $\cdots$ O($12'^{\mathrm{III}}$)	3·22	C(10) $\cdots$ O($2'$)	3·00
N(4) $\cdots$ O($10'^{\mathrm{IV}}$)	3·23	N(1) $\cdots$ O($2'$)	3·07
N(6) $\cdots$ O($10'^{\mathrm{I}}$)	3·11	N(1) $\cdots$ O($3'$)	3·23
Cu(2) $\cdots$ O($4'^{\mathrm{VI}}$)	2·78	N(2) $\cdots$ O($4'$)	3·23
O(9) $\cdots$ O($1'^{\mathrm{III}}$)	3·23	N(3) $\cdots$ O($1'^{\mathrm{III}}$)	3·19
O(10) $\cdots$ O($4'^{\mathrm{V}}$)	3·14	N(3) $\cdots$ O($3'^{\mathrm{V}}$)	3·10
O(11) $\cdots$ O($8'^{\mathrm{VI}}$)	3·24	N(4) $\cdots$ O($2'^{\mathrm{IV}}$)	3·21
O(12) $\cdots$ O($1'^{\mathrm{III}}$)	3·24	N(5) $\cdots$ O($8'^{\mathrm{IV}}$)	3·04
O(12) $\cdots$ O($4'^{\mathrm{IV}}$)	3·33	N(6) $\cdots$ O($2'$)	3·24
C(9) $\cdots$ O($1'^{\mathrm{III}}$)	2·89	N(6) $\cdots$ O($4'^{\mathrm{IV}}$)	3·06

Transformations denoted by Roman numeral superscripts

I $-x, y - \frac{1}{2}, z$
II $1 + x, y, z$
III $-x, \frac{1}{2} + y, z$
IV $x - 1, y, z$
V $1 - x, \frac{1}{2} + y, z$
VI $-x, -y, z - \frac{1}{2}$

(*c*) Compound (III)

O(9) $\cdots$ N($4'^{\mathrm{I}}$)	3·01	C(14) $\cdots$ O($2'$)	3·13
O(11) $\cdots$ N($3'^{\mathrm{II}}$)	2·93	C(14) $\cdots$ O($4'^{\mathrm{II}}$)	3·04
Zn(1) $\cdots$ O($'8$)	3·11	N(1) $\cdots$ O($3'^{\mathrm{II}}$)	3·19
Zn(2) $\cdots$ O($7'^{\mathrm{II}}$)	3·34	N(2) $\cdots$ O($1'^{\mathrm{III}}$)	3·21
O(9) $\cdots$ O($2'$)	3·25	N(3) $\cdots$ O($2'$)	3·25
O(9) $\cdots$ O($7'$)	3·21	N(3) $\cdots$ O($8'$)	3·22
O(11) $\cdots$ O($4'^{\mathrm{II}}$)	3·26	N(4) $\cdots$ O($7'^{\mathrm{II}}$)	3·02
C(13) $\cdots$ O($2'$)	2·98	N(6) $\cdots$ O($7'^{\mathrm{II}}$)	2·97
C(13) $\cdots$ O($4'^{\mathrm{II}}$)	2·99		

Transformations denoted by Roman numeral superscripts:

I $\frac{1}{2} + x, \frac{1}{2} - y, z$
II $x - \frac{1}{2}, \frac{1}{2} - y, z$
III $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} + z$

(ii) $[\{Cu(dien)\}_2(C_2O_4)](ClO_4)_2$, (II). The stereochemistry about the copper ions is square pyramidal with the oxalate oxygen atoms occupying one basal and one apical site. At both metal centres the pyramidal bases have a slight tetrahedral distortion and the metal ions are displaced towards the apical atom by *ca.* 0·15 Å [Table 5 (*b*)]. The Cu–O(apical) bonds are somewhat longer than the Cu–O(basal) bonds as is common for square planar copper(II). Copper–donor bond lengths are normal except for the Cu(1)–N(3) 1·88(1) Å, but as there are no clear chemical grounds for supposing that this bond should be short we regard this value with suspicion. Table 7 (*b*) which lists intermolecular contacts, together with Table 5 (*b*), disclose that each copper atom completes a very distorted octahedron if the perchlorate oxygen atom lying close to the tetragonal axis of each group be assumed a further donor. The distances involved [Cu(1)–O(3′) 2·96, Cu(2)–O(4″) 2·78 Å] suggest that they should be so regarded [*cf.* Cu–O 2·6 Å found in tetragonal $Cu(en)_2(ClO_4)_2$ where the ClO_4^- ions are semi-co-ordinated [33]]. The positioning of these atoms with respect to the complex cation can be seen in the molecular packing diagram [Figure 2 (*b*)], which also shows that parts of the crystal structure approximate to centrosymmetry, although it does not, particularly in the perchlorates, obey the requirements of space group *Pbcm*.

The dien ligands of the copper complex ion also show distorted *gauche* conformations of five-membered rings. Two [Cu(1), N(1), C(1), C(2), N(2) and Cu(2), N(5), C(7), C(8), N(6)] are much more asymmetric than the other two, and of the latter one ring [Cu(1), N(2), C(3), C(4), N(3)] shows very large and relatively symmetrical deviations of the carbon atoms [0·43 and −0·51 Å, Table 5 (*b*)] from the plane defined by the metal and the two donors. It is not immediately obvious why this ring is so buckled but as with (I) there is extensive hydrogen bonding involving the amine nitrogen atoms. The largest deviation from the plane occurs at the carbon atoms bonded to the secondary nitrogens [C(2), C(3) and C(6), C(7)], a feature of a number of meridionally co-ordinated dien complexes (Figure 3), which presents the situation in $[Cu(dien)_2]Br_2,H_2O$,[8] $[Cu(dien)(HCO_2)]HCO_2$,[11] $Cu(dien)(C_2O_4)$,$4H_2O$,[10] and (II). This is understandable although it is by no means obvious that it must always be so. Equally understandable is the observation that in (II) the carbon atoms bonded to the secondary nitrogens are displaced in a direction away from the apical co-ordinating atom. Figure 3 also shows the varied nature of the buckling where details are concerned, a range which is again assumed to reflect the different interatomic interactions in different crystals.

The conformations of the five-membered rings at each centre are λδ, the presence of a common nitrogen atom ensuring this arrangement in all the compounds of Figure 3.

(iii) $[\{Zn(dpt)\}_2(C_2O_4)](ClO_4)_2$, (III). The co-ordination stereochemistries at the metal centres of (III) show yet another geometry, trigonal bipyramidal, again with distortions. Values for bond lengths and angles are

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[32] Mazhur-Ul-Haque, C. N. Caughlan, and K. Emerson, *Inorg. Chem.*, 1970, **9**, 2421.

[33] Y. Komiyama and E. C. Lingafelter, *Acta Cryst.*, 1964, **17**, 1145.

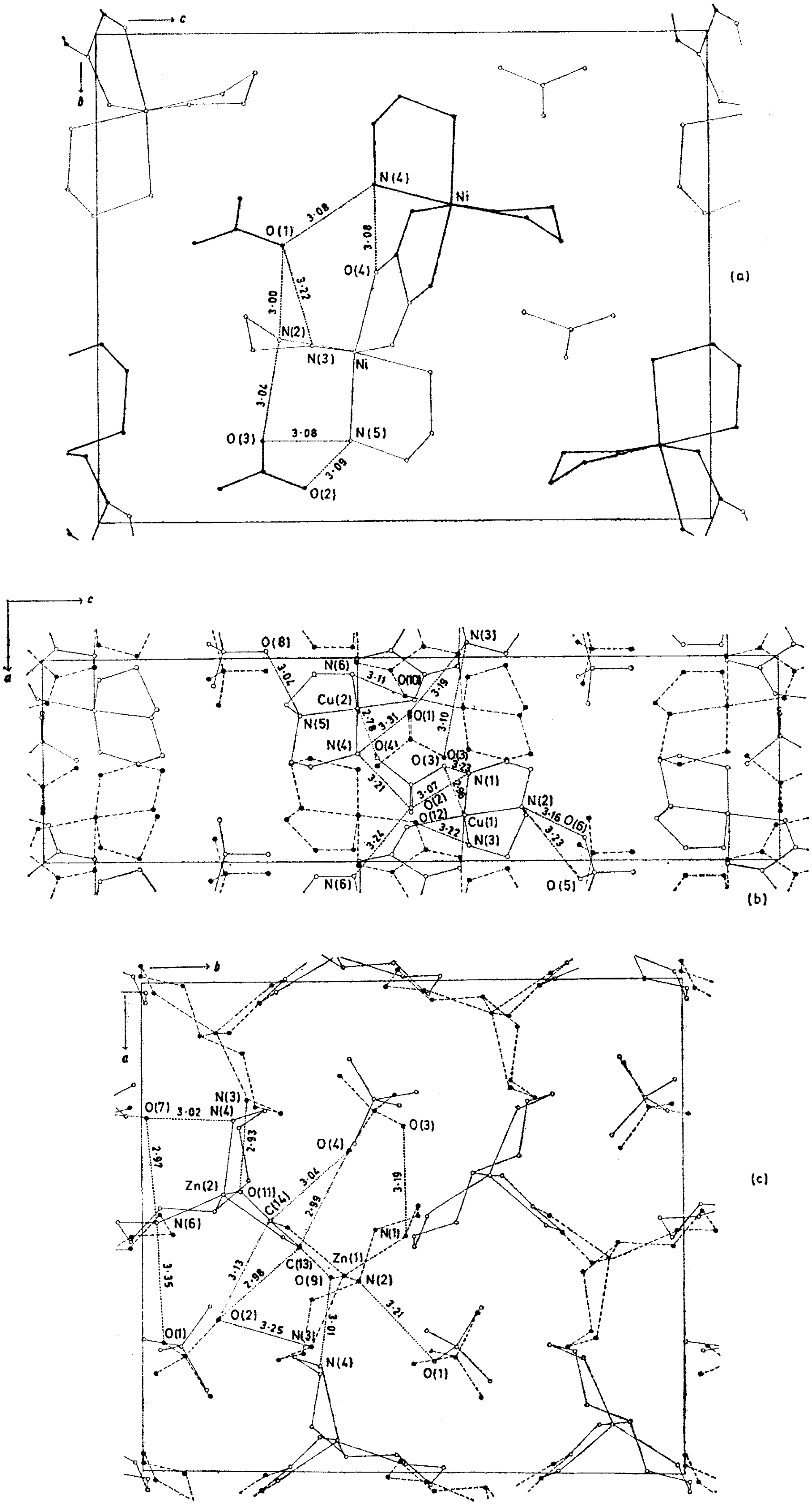

FIGURE 2 Projections of the crystal structures showing intermolecular contacts within an asymmetric unit: (a) (I) $[\{Ni(en)_2\}_2(C_2O_4)](NO_3)_2$; (b) (II) $[\{Cu(dien)\}_2(C_2O_4)](ClO_4)_2$; and (c) (III) $[\{Zn(dpt)\}_2(C_2O_4)](ClO_4)_2$

given in Table **3** (*c*) and 4 (*c*); relevant planes of best fit are quoted in Table **5** (*c*). The oxalate oxygen atoms occupy one apical and one equatorial site at each metal, the O–Zn–O chelate angle of *ca.* 80° approximating to the 90° of the bipyramid. The dpt ligands have secondary nitrogen atoms in the second apical sites, the primary amines occupying the remaining equatorial positions. This arrangement at each centre thus corresponds with the vicinal mode in octahedral co-ordination. There are, however, important differences between the metals. This is especially apparent in the angle subtended at zinc by the primary, equatorially bonded, nitrogen atoms of the dpt groups. The N(4)–Zn(2)–N(6) angle is 122° (*cf.* the 'ideal' angle of 120°) but N(1)–Zn(1)–N(3) is 145°, apparently because of the presence of a perchlorate oxygen atom, O(8), close to the equatorial plane at 3·11 Å from Zn(1). The co-ordination geometry at this centre could thus be regarded as that of a distorted octahedron in which one donor metal link is very long.

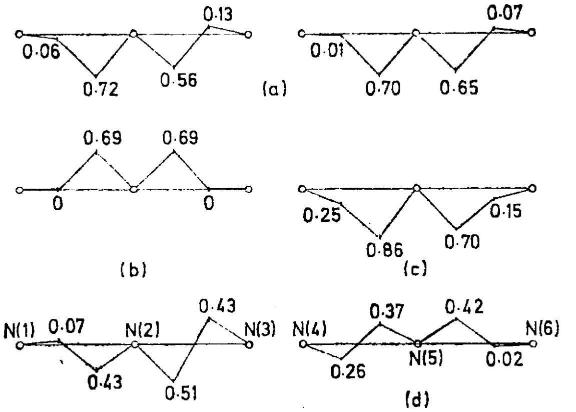

FIGURE 3 Conformations of co-ordinated diethylenetriamines: (a) Cu(dien)$_2$Br$_2$,H$_2$O, (b) [Cu(dien)(HCO$_2$)]HCO$_2$, (c) Cu(dien)(C$_2$O$_4$),4H$_2$O, and (d) [{Cu(dien)}$_2$(C$_2$O$_4$)](ClO$_4$)$_2$. Circles represent nitrogen atoms. The conformations of the chelate rings are represented by projections of the carbon atoms on to a plane which is normal to the N–M–N plane of each ring and which passes through the two N atoms of that ring. Distances (Å) from the N–M–N planes are shown

The four chelate rings formed by dpt all have the chair conformation, but their relationship within each ligand is different. At Zn(1) the chelate rings are disposed so that an approximate mirror relation exists across a plane through their common Zn–N(secondary) bond, but at Zn(2) they are approximately related by a 120° rotation about this bond. In the former, the chairs may be thought of as back-to-back in the latter as back-to-foot [see Figures 1 (*c*) and 4]. (In [Ni(dpt)$_2$](ClO$_4$)$_2$,[14] with meridional co-ordination the conformation is back-to-back.) To our knowledge this is the first reported example of non-meridional co-ordination by dpt, a circumstance not only forced by the demands of the oxalate group, but, by reducing intramolecular repulsion, also favoured by the trigonal bipyramidal geometry. In the more normal meridional bonding, which reduces intrachelate contacts, the alternatives seem to be a chair–distorted-boat conformation as in [Cu(dpt)(OAc)]ClO$_4$ [15] and the α- and β-[Co(en)(dpt)Cl]$^{2+}$ cations,[12,13] or, if a chair–chair geometry is to prevail, a significant lengthening of the metal–nitrogen bonds, as in [Ni(dpt)$_2$](ClO$_4$)$_2$. A study of models suggests that for idealised bond lengths and angles, including equal metal–nitrogen bonds of *ca.* 2·0 Å and a trigonal bipyramidal stereochemistry, the back-to-back conformation adopted at Zn(1) should be strain-free and that strain in the other back-to-foot arrangement is relieved if the metal–secondary-nitrogen bond is lengthened. The value of 2·14 Å found for the Zn(2)–N(5) bond [*cf.* 2·04 and 2·06 Å for the bonds to the primary nitrogens N(4) and N(6)] is therefore presumably to be expected. That the metal–secondary-nitrogen bond [Zn(1)–N(2)] is also significantly longer seems also to have a steric explanation, since the distortion of the equatorial angles subtended at zinc causes N(1)–Zn(1)–N(3) to be expanded to 145°. If it were 180° the donor arrangement of the amine would then be that for meridional co-ordination in the octahedral stereochemistry, a situation in which strain-free chair–chair conformations can only be achieved if the metal–secondary-nitrogen bond, or all metal–nitrogen bonds, are increased from 2·0 Å.

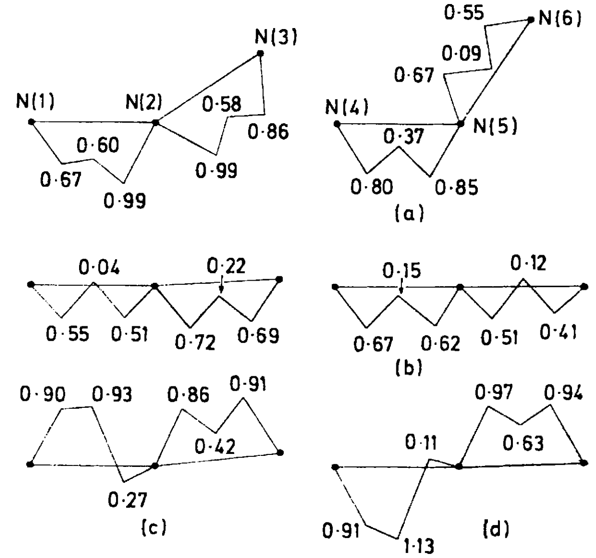

FIGURE 4 Conformations of co-ordinated dipropylenetriamines: (a) [{Zn(dpt)}$_2$(C$_2$O$_4$)](ClO$_4$)$_2$, (b) [Ni(dpt)$_2$](ClO$_4$)$_2$, (c) [Cu(dpt)(OAc)]ClO$_4$, and (d) β-[Co(en)(dpt)Cl]ZnCl$_4$. Circles represent nitrogen atoms; the observed N–N–N angle is shown. The conformations of the chelate rings are represented by projections of the carbon atoms on to a plane which is normal to the N–M–N plane of each ring and which passes through the two N atoms of that ring. Distances (Å) from the N–M–N planes are shown

This is not to suggest a cause for the lengthening of the bond lengths, indeed the reverse view is equally valid if the longer bonds to the apical nitrogen atoms be presupposed a requirement of zinc,[34,35] but to confirm a

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[35] F. W. B. Einstein and B. R. Penfold, *Acta Cryst.*, **1966**, **20**, 924.

relationship between chelate ring conformation and metal–donor distances. Both these features may be reflecting other causal factors (see later).

Structure of Anions.—The perchlorate ions of compounds (II) and (III) gave evidence that their oxygen atoms were undergoing large thermal vibrations or had equivalent static disorder. It was clear from difference-Fourier maps, however, that such disorders did not obviously require the use of a number of fractionally weighted models for the anion, although it is probable that the use of conventional ellipsoids of revolution to describe the situation was inadequate. Bond lengths are generally short, as is to be expected in the circumstances.

The nitrate ion of (I) has the expected geometry. The four atoms are coplanar (χ^2 0·101 for the plane $0{\cdot}624x - 0{\cdot}780y - 0{\cdot}046z + 0{\cdot}734 = 0$).

Hydrogen bonding and molecular packing. The hydrogen bonding is asymmetric in the sense of not including all suitable atoms, and a range of chelate ring conformations is a likely consequence. Other intermolecular forces also seem to be important and we mention $C \cdots O$ interactions in this context. Details of the hydrogen bonding in all three compounds are shown in Figure 2.

(i) $[\{Ni(en)_2\}_2(C_2O_4)](NO_3)_2$, (I). Eight non-furcated hydrogen bonds are possible and all are present, two to each nitrogen atom. By the criterion of $O \cdots N$ distances, the bond to N(3) is weaker than the rest although such a criterion is open to criticism. There are six bonds to nitrate, three to O(1) and two to O(3), and one to the oxalate oxygen atom O(4). This hydrogen-bonding network extends three-dimensionally throughout the crystal. Other forces are less readily identified from structural data but a feature present in all three compounds is the relatively close approach of the oxo-anions to the carbon atoms of the oxalate bridge [O(1) $\cdots$ C(5) 3·27 Å]. Such a requirement must interact on the hydrogen bonding and the steric interactions within the crystal.

(ii) $[\{Cu(dien)\}_2C_2O_4](ClO_4)_2$, (II). Ten hydrogen atoms are available for hydrogen bonding and twelve possible interactions are noted (setting the limit for the $H \cdots O$ at 2·5 Å). The bonding is not symmetrical as far as the two chelated amines are concerned, there being, for example, bifurcated bonds to N(2), but only one interaction with the other secondary nitrogen N(5). The primary nitrogen, N(6), has two bonds, but N(3) has three. The same situation holds for the perchlorate groups. The ion based on Cl(1) has seven hydrogen-bonding interactions whereas that based on Cl(2) has only three. It is the Cl(1) group which also interacts with the oxalate carbon [C(9) $\cdots$ O(1) 2·89, C(9) $\cdots$ O(2) 3·06, C(10) $\cdots$ O(1) 2·94, C(10) $\cdots$ O(2) 3·00 Å] and with the copper atoms [Cu(1) $\cdots$ O(3) 2·96, Cu(2) $\cdots$ O(4) 2·78 Å] and suggest that these latter interactions are more a requirement of the molecular, rather than the crystal, structure. The detailed conformation of the chelate rings will thus be a balance between the steric interference imposed by the perchlorate and the increased opportunity for hydrogen bonding presented by the close proximity of its oxygen atoms to the amines. In contrast the other perchlorate clearly has a space-filling role, completing hydrogen bonds where possible.

(iii) $[\{Zn(dpt)\}_2(C_2O_4)](ClO_4)_2$, (III). Ten non-furcated hydrogen bonds are possible and eight are present. At the Zn(2) centre the primary amines have two each, the secondary amine none; at Zn(1) the primary amine N(3) has two bonds with the other two nitrogens having one bond each. Again there is a close interaction between the perchlorate group based on Cl(1) and the oxalate bridge [C(13) $\cdots$ O(2) 2·98, C(13) $\cdots$ O(4) 2·99, C(14) $\cdots$ O(2) 3·13, C(14) $\cdots$ O(4) 3·04 Å] but this time it is the other perchlorate which bonds to a zinc atom [Zn(1) $\cdots$ O(8) 3·11 Å]. The hydrogen bonding distribution between anions is still, however, unequal at four and two respectively and again the hydrogen bonding system is three-dimensional.

As already noted the amines at each metal centre are geometrically different, the hydrogen atom on the secondary nitrogen atom being *trans* to the equatorial oxygen atom, O(10), at Zn(1) but *cis* to O(12) at Zn(2). Since this arrangement is unlikely to be a built-in requirement of the complex cation the ' inversion ' of one nitrogen must be associated with interactions in the crystal. If there were to be idealised trigonal bipyramidal geometries involving equal metal–nitrogen bond lengths at both zinc centres then the strained back-to-foot arrangement at Zn(2) would presumably need this stabilisation. However, it is the secondary nitrogen atom at Zn(1) which is hydrogen bonded, suggesting that it is the back-to-back situation which is unfavoured. This follows if longer bonds to the apical secondary nitrogens be presupposed and indicates that the ' octahedral distortion ' takes place at this centre to relieve some of the strain. It could be said, therefore, that the difference in chelate ring conformations is indeed dependent upon hydrogen bonding but that the overall geometrical relationship reflects a number of forces, not the least significant in this complex being the detailed requirements of the metal.

The interaction between the oxoanions and the carbon atoms of the oxalate bridge is also a feature of apparent significance, this time in all complexes. We assume that it is electrostatic in nature since it seems probable that the carbons will have a slight positive charge as a result of the electronegativity of their bonded (and co-ordinated) oxygen atoms.

[2/1506 *Received, 27th June, 1972*]