

Some Oxalato–Amine Complexes of Nickel(II), Copper(II), and Zinc(II)

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Preparations of the compounds $[\{\text{Ni}(1,3\text{-pn})_2\}_2\text{C}_2\text{O}_4](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, $[\{\text{Ni}(\text{dpt})\text{H}_2\text{O}\}_2\text{C}_2\text{O}_4](\text{ClO}_4)_2$, $[\{\text{Cu}(\text{dien})_2\}_2\text{C}_2\text{O}_4](\text{ClO}_4)_2$ (and hydrate), $[\{\text{Cu}(\text{dpt})\}_2\text{C}_2\text{O}_4](\text{ClO}_4)_2$, $[\{\text{Zn}(\text{en})_2\}_2\text{C}_2\text{O}_4](\text{ClO}_4)_2$, $[\{\text{Zn}(\text{dpt})\}_2\text{C}_2\text{O}_4](\text{ClO}_4)_2$, and $[\{\text{Zn}(\text{trien})\}_2\text{C}_2\text{O}_4](\text{ClO}_4)_2$, considered to have dimeric structures with bridging bichelate oxalate ions, are described. The pairs of compounds $[\{\text{M}(\text{en})_2\}_2\text{C}_2\text{O}_4](\text{ClO}_4)_2$ and $[\{\text{M}(\text{trien})\}_2\text{C}_2\text{O}_4](\text{ClO}_4)_2$ [M = Ni(II) or Zn(II)] are isostructural, whereas the pair $[\{\text{M}(\text{dpt})\}_2\text{C}_2\text{O}_4](\text{ClO}_4)_2$ [M = Cu(II) or Zn(II)] are not isostructural. The racemic isomer of the cyclic tetramine 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane forms an analogous compound, $[\{\text{Ni}(\text{tet } b)\}_2\text{C}_2\text{O}_4](\text{ClO}_4)_2$, whereas the *meso*-isomer forms only a simple oxalate, $\text{Ni}(\text{tet } a)\text{C}_2\text{O}_4$, and its trihydrate, considered to have polymeric structures with bridging, bi-unidentate oxalate ions. The compounds $[\text{Zn}(1,3\text{-pn})_2](\text{ClO}_4)_2$ and $[\text{Zn}_3(\text{trien})_4](\text{ClO}_4)_6$ were also prepared. Infrared spectra and magnetic susceptibilities ($\mu_{\text{eff}} \sim 3$ B.M. for the nickel compounds and ~ 1.8 B.M. for the copper compounds) are reported (en = diaminoethane; 1,3-pn = 1,3-diaminopropane; dien = diethylenetriamine; dpt = dipropylenetriamine; trien = triethylenetetramine).

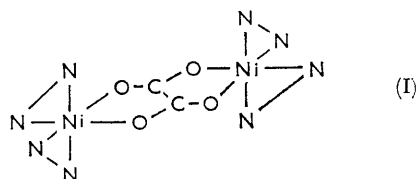
In an earlier paper,¹ the preparation of a series of oxalato-amine complexes of nickel(II), of the general formula $[\{\text{Ni}(\text{N}_4)\}_2\text{C}_2\text{O}_4](\text{ClO}_4)_2$, was described (where N_4 represents a linear or cyclic tetramine, or bis-diamine). From consideration of the infrared spectra of the oxalate ion in these compounds, dimeric structures with the oxalate ion functioning as a bridging bichelate ligand, as in

formula (I), were proposed.¹ This arrangement has since been confirmed by an X-ray crystallographic study of $[\{\text{Ni}(\text{en})_2\}_2\text{C}_2\text{O}_4](\text{NO}_3)_2$ by McCormick and Waters (en = diaminoethane).² With diethylenetriamine (= dien) a related compound $[\{\text{Ni}(\text{dien})\text{H}_2\text{O}\}_2\text{C}_2\text{O}_4](\text{ClO}_4)_2$,

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

² R. McCormick and T. N. Waters, personal communication.

with a co-ordinated water molecule replacing a co-ordinated amino-group, was described.¹ In this paper some further oxalato-amine complexes of nickel(II) with bridging bichelate oxalato-groups are described, as well



as similar compounds formed by copper(II) and zinc(II). One nickel(II) complex with a bridging bi-unidentate oxalato-group is described.

With nickel(II), the previously reported series of complexes has been extended by the preparation of the 1,3-diaminopropane (= 1,3-pn) and dipropylenetriamine (= dpt) complexes $[\{\text{Ni}(1,3\text{-pn})_2\}_2\text{C}_2\text{O}_4](\text{ClO}_4)_2$ and $[\{\text{Ni}(\text{dpt})\text{H}_2\text{O}\}_2\text{C}_2\text{O}_4](\text{ClO}_4)_2$, analogous to the previously described diaminoethane and diethylenetriamine compounds.

With copper(II), oxalato-amine derivatives have been prepared with diethylenetriamine and dipropylenetriamine, of the type $[\{\text{Cu}(\text{dien})\}_2\text{C}_2\text{O}_4](\text{ClO}_4)_2$. The infrared spectra of the oxalate ions for the nickel(II) oxalato-amine compounds, these copper(II) compounds, and the subsequently described zinc(II) oxalato-amine compounds are very similar, indicating the presence of bridging bichelate oxalate ions in all cases. There are no bands in the $\nu(\text{NH})$ region of the infrared spectra of the copper compounds characteristic of non-co-ordinated (or weakly co-ordinated) primary amino-groups, such as have been observed with some other copper(II) complexes of dipropylenetriamine and diethylenetriamine.³ The compounds are thus considered to have dimeric five-coordinate structures with bridging bichelate oxalate ions. The diethylenetriamine complex crystallises from aqueous solution above about 50° as an anhydrous form, and at room temperature as a hydrate,* which does not dehydrate at 120°. The $\nu(\text{OH})$ bands in the infrared spectrum of the hydrate are characteristic of lattice water, rather than co-ordinated or strongly hydrogen-bonded water. However, the infrared spectra of the amine in the two compounds (over the range 1500—400 cm^{-1}) are quite dissimilar, indicating different configurations of the amine molecule.

With zinc(II), the tetramine derivatives $[\{\text{Zn}(\text{en})_2\}_2\text{C}_2\text{O}_4](\text{ClO}_4)_2$ and $[\{\text{Zn}(\text{trien})\}_2\text{C}_2\text{O}_4](\text{ClO}_4)_2$ (trien = triethylenetetramine) are isostructural with their nickel(II) analogues (by X-ray powder diffraction) and hence are assigned six-coordinate structures. The triamine derivative $[\{\text{Zn}(\text{dpt})\}_2\text{C}_2\text{O}_4](\text{ClO}_4)_2$,* which presumably has five-coordinate zinc, is not isostructural with the formally analogous copper(II) compound, the

structural difference presumably being a consequence of the differing stereochemistries of the d^9 copper(II) and d^{10} zinc(II) ions. The occurrence of both five- and six-coordinate compounds with zinc(II) is a consequence of the more variable co-ordination number and geometry possible with this spherically symmetrical ion. High-spin d^8 nickel(II) is also spherically symmetrical, but shows a less flexible co-ordination pattern which can be formalised in terms of 'crystal field stabilisation' of (pseudo)octahedral co-ordination.

The cyclic tetramine C-racemic 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradecane (= tet *b*), which is known for form derivatives with the amine buckled to accommodate a chelate (see preceding paper), forms $[\{\text{Ni}(\text{tet } b)\}_2\text{C}_2\text{O}_4](\text{ClO}_4)_2$ with bridging bichelate oxalate ions.⁴ The C-*meso*-isomer (= tet *a*) for which only square-planar and *trans*-octahedral derivatives have been prepared, forms only the simple oxalate $\text{Ni}(\text{tet } a)\text{C}_2\text{O}_4$ and its trihydrate. A polymeric formulation for these compounds, with *trans*-oxalato-groups bridging planar nickel tetramine groups, is supported by: the observed triplet ground-state; the reflectance spectra which are indicative of *trans*- NiN_4O_2 co-ordination (see below); the infrared spectra of the oxalate ions which are dissimilar from ionic, chelate, and bridging bichelate oxalate (see below); and the insolubility except in solvents such as water where complete dissociation occurs giving the singlet ground-state $[\text{Ni}(\text{tet } a)]^{2+}$ cation [cf. $\text{Ni}(\text{tet } a)(\text{CH}_3\text{COO})_2$ which dissolves in a variety of organic solvents without dissociation (preceding paper)].

During this investigation the complexes $[\text{Zn}(1,3\text{-pn})_2](\text{ClO}_4)_2$ and $[\text{Zn}_3(\text{trien})_4](\text{ClO}_4)_6$ were obtained and their preparations and infrared spectra reported {cf. $[\text{Ni}_2(\text{trien})_3](\text{ClO}_4)_4$ and $[\text{Cu}(\text{trien})](\text{ClO}_4)_2$ }.⁵

Infrared Spectra.—For the compounds with bridging bichelate oxalate, the oxalate ion vibrational spectra closely resemble those of the nickel(II) compounds previously described,¹ and assignments are the same (Table 1). The oxalate spectra of $\text{Ni}(\text{tet } a)\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ and $\text{Ni}(\text{tet } a)\text{C}_2\text{O}_4$ are dissimilar from those of ionic oxalate and those of nickel(II) complexes with normal chelate and bridging bichelate oxalate (Table 2). In particular, the single $\nu_{\text{as}}(\text{O}-\text{C}-\text{O})$ and the $\delta(\text{O}-\text{C}-\text{O})$ bands are shifted to lower frequencies compared with the other types of oxalate compounds. The secondary amine $\nu(\text{NH})$ absorption of the hydrate shows two bands, a sharp strong band at 3220 and a broader band at 3160 cm^{-1} , a pattern characteristic of two non-interacting NH groups and two NH groups involved in weak hydrogen-bonding, presumably to the non-co-ordinated oxygen atom of the carboxylate group [causing a displacement to lower frequencies of the $\nu(\text{NH})$ vibration]. {A similar pattern was observed for the diacetate and diformate of $[\text{Ni}(\text{tet } a)]^{2+}$ (preceding paper)}. For the anhydrous compound a single $\nu(\text{NH})$ band at 3160 cm^{-1} implies that all NH groups are equivalent and involved in weak

* X-Ray structural studies of these compounds are in progress.²

³ N. F. Curtis, R. W. Hay, and Y. M. Curtis, *J. Chem. Soc. (A)*, 1967, 182; K. H. J. Powell and N. F. Curtis, to be published.

⁴ N. F. Curtis, *J. Chem. Soc.*, 1964, 2644.

⁵ N. F. Curtis and D. A. House, *J. Chem. Soc.*, 1965, 6194.

TABLE 1
Infrared spectra of compounds with bridging bidentate oxalate ions (cm.⁻¹)

Cation ^a	$\nu(\text{NH})$				$\delta(\text{NH}_2)$	$\nu_{\text{as}}(\text{OCO})$	$\nu_{\text{s}}(\text{OCO})$	$\delta(\text{OCO})$
	3339s	3290s	3265sh	3175m				
Ni(1,3-pn) ₂ ^{b,c}	3325sh			3092w	1610sh	1645vs	1350m	792m
Ni(dpt)H ₂ O ^d	3337s,br	3298sh	3270m,sp	3178s,br	1598m	1640vs	1308m	800m
Ni(tet b) ^e		3282s						
Cu(dien)	3352s,br	3275s,sp	3260m,sp		1595m	1648vs	1313m	790m
Cu(dien) ^{b,f}	3353s	3300s	3265s	3174m	1590m	1650vs	1297m	795m
Cu(dpt)	3336s	3300s	3245s,br	3155sh	1583m	1642vs	1305m	783m
Zn(en) ₂	3371s,sp	3313s,sp	3265s	3158w	1581m	1650vs	1313m	792m
Zn(trien)	3344s,sp		3272m	3178m	1610m			
Zn(dpt)	3360s	3305s	3257s	3163m	1595m	1650vs	1312m	792m
	3338s	3285s	3259m,sp	3158w	1585m	1652vs	1318m	798m
				3112vw				

^a All formulae of type $\{[\text{cation}]_2\text{C}_2\text{O}_4\}(\text{ClO}_4)_2$. ^b Hydrate. ^c $\nu(\text{OH})$ 3610m and 3535m,sh. ^d $\nu(\text{OH})$ 3520s. ^e Plus bands due to oxalate at 1483, 965, and 912. ^f $\nu(\text{OH})$ 3642m,br and 3562m,br.

hydrogen-bonding. The $\nu(\text{OH})$ band of the hydrate consists of a single broad band at *ca.* 3425 cm.⁻¹, indicative of hydrogen-bonding.

TABLE 2
Infrared spectra of the oxalate ion (cm.⁻¹) ^a

Assignment ^b	Bridging bidentate ^{b,d}		Chelate ^{b,e}	Bridging bi-unidentate	
	Ionic ^{b,c}	1640vs		1610vs	1567vs ^f
$\nu_{\text{as}}(\text{OCO})$	—	—	1720sh	—	—
$\nu_{\text{s}}(\text{OCO})$	—	—	1433s	—	—
	1335s	1355w	—	1351m	1365m
	1316s	1315m	1305s	1300s	1310s
$\delta(\text{OCO})$	774s	795m	775s	740s	760s

^a Omitting some shoulders reported in ref. 1. ^b See ref. 1. ^c $\text{Na}_2\text{C}_2\text{O}_4$. ^d Typical values, see Table 1. ^e $\text{K}_2\text{Ni}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$. ^f $\text{Ni}(\text{tet } a)\text{C}_2\text{O}_4$. ^g $\text{Ni}(\text{tet } a)\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$.

Magnetic Susceptibilities.—The magnetic susceptibilities (Table 3) of the nickel(II) and copper(II) compounds are 'normal' for two and one unpaired electrons respectively. The normal magnetic moment for the copper(II)

as observed for other copper(II) carboxylate derivatives, including copper(II) oxalate.⁶

Metal-ion Spectra (Table 3).—The nickel(II) compounds with NiN_4O_2 co-ordination have reflectance spectra similar to those of the nitrate-amine nickel(II) compounds previously described.⁷ Thus, the compounds formulated with *cis*-structures have three-band spectra, as for Ni(II) on O_h symmetry, while for the *trans*-compounds the lowest-energy band (derived from ${}^3T_{2g} \leftarrow {}^3A_{1g}$ of O_h) is split into two components, ${}^3E_g \leftarrow {}^3B_{1g}$ and ${}^3B_{2g} \leftarrow {}^3B_{1g}$.⁸ The NiN_3O_3 compounds, *e.g.*, $\{[\text{Ni}(\text{dien})\text{H}_2\text{O}]_2\text{C}_2\text{O}_4\}(\text{ClO}_4)_2$, also have the three-band spectra, with the bands displaced to lower frequencies. The copper(II) compounds have very broad absorption bands, a feature indicating a departure from square-planar co-ordination.

EXPERIMENTAL

Commercial amines were used without purification. Compounds used were the normal hydrates, *e.g.*, $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$, etc.

TABLE 3
Reflectance spectra and magnetic susceptibilities

Compound	$10^6 \chi_d (\text{°K})$	μ_{eff} (B.M.) ^a	Band maxima $\times 10^{-3}$ (cm. ⁻¹)		
			10-8	17-6	27-2 ^c
$\{[\text{Ni}(\text{en})_2]\text{C}_2\text{O}_4\}(\text{ClO}_4)_2$ ^b		3-00 ^b	10-7	17-5	27-7
$\{[\text{Ni}(1,3\text{-pn})_2]\text{C}_2\text{O}_4\}(\text{ClO}_4)_2$	9-80 (297)	2-93	10-1	16-8	26-8
$\{[\text{Ni}(\text{dien})\text{H}_2\text{O}]_2\text{C}_2\text{O}_4\}(\text{ClO}_4)_2$ ^b		2-89 ^b	10-1	16-8	26-8
$\{[\text{Ni}(\text{dpt})\text{H}_2\text{O}]_2\text{C}_2\text{O}_4\}(\text{ClO}_4)_2$	10-8 (295)	3-05	10-8	(8-6sh)	17-0
$\{[\text{Ni}(\text{tet } b)]_2\text{C}_2\text{O}_4\}(\text{ClO}_4)_2$	7-31 (291)	2-95	10-1	17-2	27-2
$\text{Ni}(\text{tet } a)\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$	8-32 (293)	3-15	9-1	14-8br	18-6
$\{[\text{Cu}(\text{dien})]\text{C}_2\text{O}_4\}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$				15-1br ^e	28-4 ^{d,e}
$\{[\text{Cu}(\text{dpt})]\text{C}_2\text{O}_4\}(\text{ClO}_4)_2$	4-22 (293)	1-90		15-6br	

^a Calculated with corrections for diamagnetism and for T.I.P., assumed equal to 60×10^{-6} c.g.s.u./mole for the copper(II) compounds, and 120×10^{-6} c.g.s.u./mole for the nickel(II) compounds. ^b From ref. 1. ^c Assignments. In O_h symmetry the triplet ground-state nickel(II) ion has a three-band absorption spectrum corresponding to the transitions ${}^3T_{1g} \leftarrow {}^3A_{1g}$, ${}^3T_{2g}(F) \leftarrow {}^3A_{2g}$, and ${}^3T_{2g}(P) \leftarrow {}^3A_{2g}$. For *cis*- NiN_4O_2 compounds the three-band spectrum remains. ^d For *trans*- NiN_4O_2 compounds the lowest-energy band is split into two components, ${}^3E_g \leftarrow {}^3B_{1g}$ and ${}^3B_{2g} \leftarrow {}^3B_{1g}$. ^e The reflectance spectrum of the anhydrous compound is very similar.

compounds indicates that a bridging bichelate oxalate ion does not provide a suitable spin-coupling mechanism,

μ -Oxalato-tetrakis-(1,3-diaminopropane)dinickel(II) Perchlorate Monohydrate, $\{[\text{Ni}(1,3\text{-pn})_2]\text{C}_2\text{O}_4\}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$.—

⁶ L. Dubicki, C. M. Harris, E. Kokot, and R. L. Martin, *Inorg. Chem.*, 1966, 5, 93, and references therein.

⁷ N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, 1965, 4, 804.

⁸ D. A. Rowley and R. S. Drago, *Inorg. Chem.*, 1967, 6, 1092.

Nickel perchlorate (5 g.) dissolved in hot water was added to a hot aqueous solution of sodium oxalate (1 g.) and 1,3-diaminopropane (3 g.). The blue-violet *product* was filtered off from the cold solution and washed with cold water, followed by ethanol (Found: C, 23.4; H, 5.9; N, 16.0. $C_{14}H_{42}Cl_2N_6Ni_2O_{13}$ requires C, 23.3; H, 5.9; Ni, 16.3%).

μ -Oxalato-diaquobis(dipropylenetriamine)dinickel(II) Perchlorate, $[\{Ni(dpt)H_2O\}_2C_2O_4](ClO_4)_2$.—Bis(dipropylenetriamine)nickel(II) perchlorate (5 g.) and oxalic acid (0.5 g.) were each dissolved in small volumes of hot water and the solutions mixed. The blue *product* was filtered off from the cold solution and washed with cold water followed by ethanol (Found: C, 24.3; H, 5.7; N, 16.6. $C_{14}H_{36}Cl_2N_6Ni_2O_{14}$ requires C, 23.9; H, 5.5; Ni, 16.7%).

Oxalato(C-meso-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) and Trihydrate, $Ni(tet a)C_2O_4$ and $Ni(tet a)C_2O_4 \cdot 3H_2O$.—Potassium oxalate (3 g.) was added to a hot concentrated aqueous solution of the chloride of $[Ni(tet a)]^{2+}$ (5 g.).⁷ The mauve crystalline *trihydrate* was filtered off from the cold solution and recrystallised from a small volume of hot water. The *product* was filtered from the cold solution and washed with methanol (Found: C, 45.2; H, 9.3; Ni, 12.2. $C_{18}H_{42}N_4NiO_7$ requires C, 44.7; H, 8.8; Ni, 12.1%); weight loss at 110°, 11.0; $-3H_2O$ requires 11.1%. The anhydrous *compound* was prepared by heating the hydrate at 110° to constant weight.

μ -Oxalato-bis(diethylenetriamine)dicopper(II) Perchlorate and Monohydrate, $[\{Cu(dien)\}_2C_2O_4](ClO_4)_2$ and $[\{Cu(dien)\}_2C_2O_4](ClO_4)_2 \cdot H_2O$.—A hot aqueous solution of sodium oxalate (3.2 g. in 30 ml.) was added to a hot aqueous solution prepared by addition of copper perchlorate (8 g. in 10 ml.) to aqueous diethylenetriamine (2.7 g. in 10 ml.). The blue crystalline *product* was filtered off from the cold solution and washed with a little cold water. The anhydrous *product* was obtained by recrystallisation from hot water, and filtering off the crystals when the solution temperature fell to 50°. The *hydrate* was obtained by evaporation of an aqueous solution at room temperature (Found for anhydrous salt: C, 19.4; H, 4.2; Cu, 20.5. $C_{10}H_{26}Cl_2Cu_2N_6O_{10}$ requires C, 19.4; H, 4.2; Cu, 20.5%. Found for hydrate: C, 19.2; H, 4.3; Cu, 20.0. $C_{10}H_{28}Cl_2Cu_2N_6O_{11}$ requires C, 18.9; H, 4.4; Cu, 20.0%).

μ -Oxalato-bis(dipropylenetriamine)dicopper(II) Perchlorate, $[\{Cu(dpt)\}_2C_2O_4](ClO_4)_2$.—Sodium oxalate (0.6 g.) was added to a hot aqueous solution of bis(dipropylenetriamine)copper(II) perchlorate. The solution was filtered while hot and the blue crystalline *product* was filtered off from the cold solution and washed with a little cold water, followed by ethanol (Found: C, 25.3; H, 5.2; Cu, 18.8. $C_{14}H_{34}Cl_2Cu_2N_6O_{12}$ requires C, 24.9; H, 5.1; Cu, 18.8%).

μ -Oxalato-tetrakis(diaminoethane)dizinc(II) Perchlorate, $[\{Zn(en)\}_2C_2O_4](ClO_4)_2$.—Zinc perchlorate tetrahydrate (3.4 g.) was added to a hot aqueous solution of diaminoethane

(1.3 g.) and sodium oxalate (0.8 g.). The solution was heated until any initially formed precipitate had dissolved, and filtered while hot. The white crystalline *product* was filtered off from the cold solution and washed with a little cold water, followed by ethanol (Found: C, 18.4; H, 5.4; Zn, 19.8. $C_{10}H_{34}Cl_2N_8O_{12}Zn_2$ requires C, 18.2; H, 5.2; Zn, 19.9%).

μ -Oxalato-bis(dipropylenetriamine)dizinc(II) Perchlorate, $[\{Zn(dpt)\}_2C_2O_4](ClO_4)_2$.—A solution of zinc perchlorate (5 g.) in methanol (10 ml.) was added to a solution of dipropylenetriamine (4 g.) and oxalic acid (1 g.) in water (10 ml.). The white crystalline *product* was filtered off and washed with a little cold water, followed by ethanol (Found: C, 24.7; H, 5.1; Zn, 19.3. $C_{14}H_{34}Cl_2N_8O_{12}Zn_2$ requires C, 24.7; H, 5.0; Zn, 19.2%). Attempts to prepare a diethylenetriamine analogue were unsuccessful.

μ -Oxalato-bis(triethylenetetramine)dizinc(II) Perchlorate, $[\{Zn(trien)\}_2C_2O_4](ClO_4)_2$.—Zinc perchlorate (7 g.) dissolved in a small volume of water was slowly added to a hot solution of triethylenetetramine (5 g.) in about 20 ml. of water. Sodium oxalate (1.5 g.) dissolved in a small volume of hot water was then added and the solution quickly filtered. The white crystalline *product* was filtered off from the cold solution and washed with a little cold water, followed by ethanol (Found: C, 17.7; H, 5.0; Zn, 15.8. $C_{14}H_{36}Cl_2N_8O_{12}Zn_2$ requires C, 17.5; H, 4.9; Zn, 15.8%).

Tetrakis(triethylenetetramine)trizinc(II) Perchlorate, $[Zn_3(trien)_4](ClO_4)_6$.—As for the previous preparation, but omitting the sodium oxalate (Found: C, 21.2; H, 5.3; Zn, 14.3; second preparation: C, 21.3; H, 5.4. $C_{24}H_{72}Cl_6N_{16}O_{24}Zn_3$ requires C, 20.9; H, 5.3; Zn, 14.2%); $\nu(NH)$ 3337s, 3320sh, 3296s, 3270sh, and 3164w; $\delta(NH_2)$ 1592m.

Bis-(1,3-diaminopropane)zinc(II) Perchlorate, $[Zn(1,3-pn)_2](ClO_4)_2$.—Zinc perchlorate dissolved in methanol was added to a hot solution of 1,3-diaminopropane in methanol (1:3 mole ratio) and the solution filtered while hot. The white crystalline *product* was filtered off from the cold solution and recrystallised from hot methanol (Found: C, 17.7; H, 5.0; Zn, 15.8. $C_6H_{20}Cl_2N_4O_8Zn$ requires C, 17.5; H, 4.9; Zn, 15.8%); $\nu(NH)$ 3315s, 3270s, 3170m, and 3075w; $\delta(NH_2)$ 1580m. Attempts to prepare zinc-(1,3-diaminopropane)-oxalato-derivatives were not successful.

Analysis.—Copper, nickel, and zinc were determined after decomposition of the complexes by boiling peroxydisulphate solution, copper and nickel gravimetrically, and zinc volumetrically using EDTA.

Finance from the Research Grants Committee of the New Zealand University Grants Committee is gratefully acknowledged.

[7/1699 Received, December 28th, 1967]