Inorganica Chimica Acta, 130 (1987) 251–257

Metal Ion Size Selectivity in Ligands with Groups Containing the Neutral Oxygen Donor Atom. A Crystallographic and Thermodynamic Study

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(Received July 9, 1986; revised December 11, 1986)

Abstract

The coordinating properties of open-chain ligands containing alcoholic or ethereal oxygen donors are examined. Addition of oxygen donors usually leads to complex stabilisation for large metal ions (Pb^{2+}, Cd^{2+}) and to less favourable effects on complex stability for small metal ions (Cu^{2+}, Ni^{2+}). The formation constants of these metal ions with the set of ligands $RN(CH_2CHOH{\cdot}CH_3)_2$ where R is –H, $-CH_2CHOH{\cdot}CH_3$, $-CH_2CH_2OCH_3$, $-CH_2CH_2OCH_2$-CH_2OH, and $-CH_2-CHOCH_2CH_2CH_2$ are reported. The largest stabilisation for each case where R is an O-donor group relative to R = H occurs for Pb^{2+}, the largest metal ion, while Cu^{2+}, the smallest metal ion, shows the smallest stabilisation. The crystal structure of $[Ni(HOCH_2CH_2NHCH_2CH_2NH_2)_2]$-$(NO_3)_2$ is reported. The space group is $P\bar{1}$, with cell constants $a = 13.098(3)$, $b = 8.737(4)$, and $c = 7.746(3)$ Å, $\alpha = 112.66(3)$, $\beta = 90.65(3)$, and $\gamma = 85.03(2)$, and $Z = 2$. Disorder of the nitrate anions hindered refinement, with the result that a final conventional R factor of 0.0903 was achieved. The Ni–N bond lengths average 2.06(1) (secondary nitrogen) and 2.10(2) (primary nitrogen). The Ni–O bond lengths are rather long, averaging 2.15(1) Å, which is used to support the idea that steric effects are responsible for destabilising the complexes of small metal ions such as Ni(II) when neutral oxygen donors are present.

Introduction

The crown ethers, and their ability to complex large metal ions, appeared quite unprecedented when first discovered by Pedersen [1]. Prior to this, ligands bearing the neutral oxygen donor in the form of alcoholic or ethereal groups had been investigated, and had not appeared to show any interesting complexing properties. Thus, for example, metal ions such as Cu^{II}, Ni^{II}, or Zn^{II} show a decrease, or little change, in complex stability [2] when hydroxyethyl groups are added to L_1 to give L_2 (Fig. 1). The moderately large metal ion Cd^{2+} shows a strong increase in complex stability in making the same change in ligand [2]. Had this result been followed up with studies on metal ions outside the above set, which is the set of metal ions usually studied with amine ligands, the complexing properties of the crown ethers may have been predicted rather than

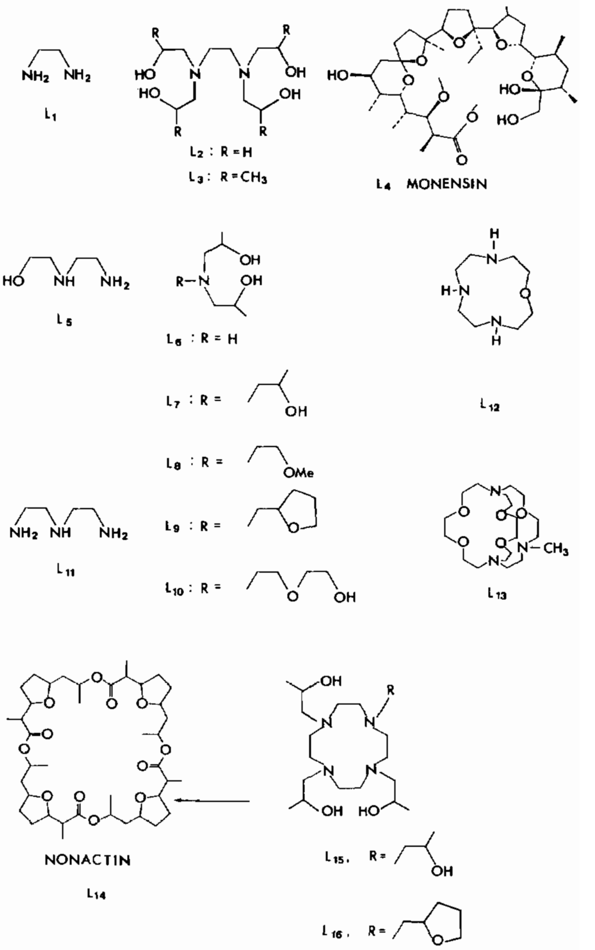

Fig. 1. Ligands discussed in this paper.

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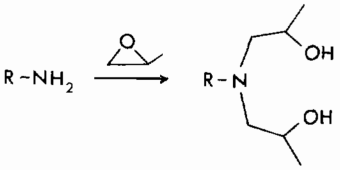
discovered by accident. Thus it was found [3] that there was an even larger increase in complex stability for Pb^{2+} in passing from L_1 to L_3, and that L_3 complexes Ca^{2+} and La^{3+}, whereas L_1 does not complex the latter ions in aqueous solution. From a comparison of L_1 and L_3 complex stabilities, as well as other ligands with neutral oxygen donors, including macrocycles, it was concluded [4] that metal ion size determined the response to the neutral oxygen donor. Thus unlike small metal ions, large metal ions respond to added neutral oxygen donor groups with increased complex stability, and also complex well with ligands containing only oxygen donors, such as the crown ethers. A large family of ligands exist which contain only neutral oxygen donor atoms, namely the monensin family of antibiotics, which successfully complex large metal ions without having a cyclic structure. These ligands, such as monensin, L_4, have predominantly tetrahydrofuran (THF) donor groups.

In this paper we attempt to address two problems relating to the neutral oxygen donor atom. Firstly, why should small metal ions show a decrease in complex stability on addition of groups bearing neutral oxygen donors? We previously suggested [3, 4] that there is a balance between the favourable inductive effects of the alkyl bridging group, and the steric strain produced, on adding a hydroxyalkyl group to an existing ligand. In the case of small metal ions, the more sterically crowded coordination sphere leads to the steric destabilisation effects dominating, so that a nett decrease in complex stability occurs. Crystal structures such as those of $[Cu(L5)_2](ClO_4)_2$ [5] and $[Cu(TRISH_{-1})(TRIS)]_2CL_2$ [6] (TRIS = 2-amino-2-(hydroxymethyl)-1,3-propanediol) have been reported, but Jahn–Teller distortion of the copper ion makes the Cu–N and Cu–O bond length deformations difficult to interpret in terms of this idea. We thus report in this paper the crystal structure of $[Ni(L_5)_2](NO_3)_2$ which should give us an indication of the amount of steric strain in terms of Ni–O and Ni–N bond length deformation, and distortion of the bond angles around the metal ion. The second point we wish to address here is what effect the nature of the group bearing the oxygen donor atom has on complex stability, and ability to discriminate between metal ions on the basis of their size. For example, does the presence of the THF group in the monensin family of antibiotics confer any greater selectivity than would be found for similar ligands having simple ethereal groups in place of the bulky THF groups? In an attempt to answer this question we have synthesized a set of ligands all based on the di-isopropanolamine group, which are L_6 to L_{10}, with neutral oxygens held in a simple hydroxyalkyl group (L_7), a methoxy group (L_8), a THF group (L_9), and a more extended hydroxyalkyl-oxyalkyl group (L_{10}) to see how these affect complex stability and selectivity for metal ions. We report here the formation constants of this set of ligands complexed to Cu^{2+}, Ni^{2+}, Cd^{2+}, and Pb^{2+}.

Experimental

Materials

All the ligands were prepared by the procedure outlined in the reaction scheme (Scheme 1). The amine (100 mmol) was dissolved in ethanol (30 ml) in a round-bottomed flask. An excess of propylene oxide was added and the contents of the flask stirred for four days. The solvent was removed under vacuum to yield the product in greater than 98% yield. The products were purified by distillation under reduced pressure to yield clear oils. *Anal.* L_7, Found: C, 56.31; H, 11.00; N, 7.31. Calc. for $C_9H_{27}NO_3$: C, 56.50; H, 10.99; N, 7.32%. L_8, Found: C, 56.67; H, 10.90; N, 7.13. Calc. for $C_9H_{27}NO_3$: C, 56.50; H, 10.99; N, 7.32%. L_9, Found: C, 61.10; H, 10.76; N, 6.39. Calc. for $C_{11}H_{23}NO_3$: C, 60.80; H, 10.67; N, 6.45%. L_{10}, Found: C, 54.39; H, 10.27; N, 6.34. Calc. for $C_{10}H_{23}NO_4$: C, 54.27; H, 10.48; N, 6.33%. Stock solutions of the ligands were made up in 0.1 M $NaNO_3$ and standardised by titration with acid. The ligand L_6 was obtained from Aldrich, and found to be better than 99% pure on titration with acid. Stock solutions of the metal ions as their nitrate salts were made up and standardised by routine procedures.



Scheme 1.

Potentiometric Studies

These were carried out using a pHM84 radiometer pH meter in a cell thermostatted at 25 °C. Three titrations were performed at 0.1 M dilution, each with excess ligand, excess metal and with equimolar ligand to metal ratios. Electrodes were calibrated by titrating neutral solutions with 0.05 M HNO_3 in the pH range: 3.3 to 2.3, and by calculating the Nernstian intercept, fixing the Nernstian slope at 95.16 mV. Analysis of the titration data to yield the equilibrium constant values shown in Table I was carried out using the computer program MINIQUAD [7], as well as the program EQUILIBRIA [8].

X-ray Crystallography

Crystals of $[Ni(L_5)_2](NO_3)_2$ were kindly donated to us by B. Martincigh of the University of Natal. A blue crystal of dimensions 0.2 × 0.5 × 0.5 mm was

TABLE I. Formation and Protonation Constants for Ligands Derived from Di-2-hydroxypropylamine at 25 °C in 0. 1 mol dm^{-3} $NaNO_3$

Ligand[a]	Lewis acid	Equilibrium[b]	log K[c]
L_6	H^+	$L + H^+ \rightleftharpoons LH^+$	8.862(1)
(R = H)	Cu^{2+}	$M + L \rightleftharpoons ML$	4.58(2)
		$ML + OH^- \rightleftharpoons MLOH^-$	7.18(6)
	Ni^{2+}	$M + L \rightleftharpoons ML$	2.86(1)
		$ML + OH^- \rightleftharpoons MLOH^-$	4.89(5)
	Cd^{2+}	$M + L \rightleftharpoons ML$	2.31(2)
	Pb^{2+}	$M + L \rightleftharpoons ML$	2.70(5)
L_7	H^+	$L + H^+ \rightleftharpoons LH^+$	7.905(2)
($R = CH_2CHOH{\cdot}CH_3$)	Cu^{2+}	$M + L \rightleftharpoons ML$	4.97(1)
		$ML + OH^- \rightleftharpoons MLOH^-$	7.53(1)
	Ni^{2+}	$M + L \rightleftharpoons ML$	3.46(1)
	Cd^{2+}	$M + L \rightleftharpoons ML$	2.31(2)
	Pb^{2+}	$M + L \rightleftharpoons ML$	3.62(1)
		$ML + OH^- \rightleftharpoons MLOH^-$	6.76(1)
L_8	H^+	$H^+ + L \rightleftharpoons HL^+$	7.813(1)
($R = CH_2CH_2OCH_3$)	Cu^{2+}	$M + L \rightleftharpoons ML$	4.57(1)
		$ML + OH^- \rightleftharpoons MLOH$	7.40(2)
	Ni^{2+}	$M + L \rightleftharpoons ML$	2.83(1)
	Cd^{2+}	$M + L \rightleftharpoons ML$	2.57(1)
	Pb^{2+}	$M + L \rightleftharpoons ML$	3.22(1)
		$ML + OH^- \rightleftharpoons MLOH^-$	6.66(2)
L_9	H^+	$H^+ + L \rightleftharpoons HL^+$	7.797(1)
($R = CH_2\overline{CHOCH_2CH_2CH_2}$)	Cu^{2+}	$M + L \rightleftharpoons ML$	4.66(1)
		$ML + OH^- \rightleftharpoons MLOH^-$	7.52(1)
	Ni^{2}	$M + L \rightleftharpoons ML$	3.06(4)
	Cd^{2+}	$M + L \rightleftharpoons ML$	2.81(1)
	Pb^{2+}	$M + L \rightleftharpoons ML$	3.65(1)
		$ML + OH^- \rightleftharpoons MLOH^-$	6.68(1)
L_{10}	H^+	$H^+ + L \rightleftharpoons HL^+$	7.862(1)
($R = CH_2CH_2OCH_2CH_2OH$)	Cu^{2+}	$M + L \rightleftharpoons ML$	4.35(1)
		$ML + OH^- \rightleftharpoons MLOH$	7.57(1)
	Ni^{2+}	$M + L \rightleftharpoons ML$	2.64(1)
	Cd^{2+}	$M + L \rightleftharpoons ML$	3.12(1)
	Pb^{2+}	$M + L \rightleftharpoons ML$	3.65(1)
		$ML + OH^- \rightleftharpoons MLOH^-$	6.57(2)

[a] For structure of ligands, see Fig. 1. [b] For simplicity, charges on metal ions have been omitted. [c] Figures in parentheses are standard deviations indicated by the program MINIQUAD [7].

used for preliminary investigations using the Weissenberg technique, and for data collection. The density, D_m, was determined by suspension in dichloroethane/dibromoethane mixtures. Diffraction data was collected on a Phillips PW 1100 four circle diffractometer equipped with an incident beam monochromator. The structure was solved and refined using the program SHELX [9]. No corrections over and above those for background and Lorentz polarisation were made. Equivalent reflections were merged, and a $3\sigma(F)$ cutoff was effected. Unit weights were used in the least squares refinement. Most hydrogen atoms were located on a Fourier difference map, but some attached to oxygen and nitrogen were placed in geometrically calculated positions. The thermal parameters of all non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were refined with common thermal parameters. The residual electron density nowhere exceeded 0.5 e $Å^{-3}$, except for a single peak of 1.33 e $Å^{-3}$ near the metal ions. The nitrate ions were disordered, which hindered refinement, and contributed to the rather high final conventional R factor. Attempts were made to resolve the disordered nitrates, without success. The disorder is thus masked by the rather large thermal parameters

TABLE II. Crystal Data for $[Ni(NH_2CH_2CH_2NHCH_2CH_2OH)_2](NO_3)_2$

Formula	$NiC_8H_{24}N_6O_8$
M_r	391.024
Space group	$P\bar{1}$
a (Å)	13.098(3)
b (Å)	8.737(4)
c (Å)	7.46(3)
α (°)	112.66(3)
β (°)	90.65(3)
γ (°)	85.03(2)
V (Å^3)	814.69
Z	2
D_m (g/ml)	1.58
D_c (g/ml)	1.59
Scan mode	$\omega - 2\theta$
Range (°)	$3 < \theta < 60$
Scan width (°)	1.6
Scan speed (°/s)	0.064
μ (cm^{-1})	21.7
Wavelength (nm)	1.5418 (Cu Kα)
F(000)	410.00
Number reflections ($F > 3\sigma$)	2419
Final R	0.0903

TABLE III. Bond Lengths (Å) and Angles (°) (e.s.d.s in parentheses)[a]

$[Ni(NH_2CH_2CH_2NHCH_2CH_2OH)_2]$ cation			
Ni–O11	2.162(5)	Ni–O21	2.136(5)
Ni–N11	2.049(7)	Ni–N21	2.064(8)
Ni–N12	2.08(1)	Ni–N22	2.121(7)
O11–C11	1.44(1)	O21–C21	1.42(1)
C1–C12	1.48(2)	C21–C22	1.54(2)
C12–N11	1.46(1)	C22–N21	1.45(1)
N11–C13	1.45(1)	N21–C23	1.49(1)
C13–C14	1.51(1)	C23–C24	1.49(1)
C14–N12	1.47(2)	C24–N22	1.48(1)
Ni–O11–C11	109.8(5)	Ni–O21–C21	111.2(5)
Ni–N11–C12	107.5(6)	Ni–N21–C22	109.2(5)
Ni–N11–C13	106.7(5)	Ni–N21–C23	106.4(5)
Ni–N12–C14	110.4(5)	Ni–N22–C24	108.0(5)
O11–Ni–N11	80.8(2)	O21–Ni–N21	80.4(2)
O11–Ni–N12	163.0(3)	O21–Ni–N22	161.5(3)
N11–Ni–N12	82.3(3)	N21–Ni–N22	83.0(3)
O11–Ni–O21	88.7(2)		
O11–Ni–N21	95.7(2)	O21–Ni–N11	96.0(2)
O11–Ni–N22	85.0(2)	O21–Ni–N12	94.6(3)
N11–Ni–N22	100.1(3)	N21–Ni–N12	101.3(3)
N12–Ni–N22	96.5(3)		
O11–C11–C12	108.9(7)	O21–C21–C22	107.7(7)
N11–C12–C11	110.8(7)	N21–C22–C21	108.4(8)
N11–C13–C14	109.6(8)	N21–C23–C24	107.9(9)
N12–C14–C13	109.5(9)	N22–C24–C23	110.6(7)
Nitrates			
N31–O31	1.25(1)	N41–O41	1.231(8)
N31–O32	1.21(1)	N41–O42	1.22(1)
N31–O33	1.23(1)	N41–O43	1.23(1)
O31–N31–O32	121.1(8)	O41–N41–N42	122.1(7)
O31–N31–O33	117.3(9)	O41–N41–N43	120.8(8)
O32–N31–N33	121.6(9)	O42–N41–O43	117.0(7)

[a] For key to numbering scheme, see Fig. 4.

for the nitrates. The relevant crystal data are seen in Table II, bond lengths and angles in Table III and fractional coordinates for atomic positions in Table IV. See also 'Supplementary Material'.

Results and Discussion

It was previously shown [3, 4] that there is a relationship between the ionic radius of the metal ion, and the response of the stability of the complex formed in passing from the parent amine to the ligand derived from this parent by adding neutral oxygen donors to it. This type of relationship is usually reasonably linear, as seen in Fig. 2. The very simplest type of relationship is that seen for L_1 and L_5 in Fig. 2. Plotting $\Delta \log K$, the difference in stability between the L_1 and L_5 complex of each metal ion, against its ionic radius [10], a very flat response is found. The change in passing from L_1 to L_5 is small since adding a single hydroxyethyl group is the least sterically demanding way in which a neutral oxygen donor can be added to an amine. If we incorporate the oxygen into a macrocyclic ring, as is the case in passing from L_{11} to L_{12}, we see (Fig. 2) that there is a much sharper response in $\Delta \log K$ to increase in ionic radius, as evidenced by the steeper slope of its relationship with ionic radius. If we drastically modify L_{11} to give the cryptand L_{13}, we see in Fig. 2 that the relationship of $\Delta \log K$ with ionic radius of metal ion now has a very steep slope indeed. This is a general result, that the more neutral oxygen donor groups we add to an amine, the more the complex stability tilts in favour of large metal ions.

The complex stability also tilts more steeply in favour of metal ions if the structural rigidity of the ligand is increased along the series open-chain < macrocyclic < macrobicyclic. Exceptions to this pattern of behaviour appear to occur only in very small ligands, where steric strain is low. This is in fact an important clue to the origin of the size-dependence observed in the presence of oxygen donors. By analogy with the strength of hydration, we would expect the strength of interaction of a metal ion with groups bearing neutral oxygen donors to increase as the size of the metal ion decreased. However, the steric crowding around the metal ion also increases as the size of the metal ion decreases. Thus the observed effect on complex stability will be the nett result of the balance between the increasing metal–oxygen bond strength as the size of the metal ion decreases, and the increasing steric strain brought about by steric crowding. Only for very small ligands does addition of neutral oxygen donors not cause de-

TABLE IV. Final Least-squares Fractional Coordinates (e.s.d.s in parenthesis)

Atom	*x*	*y*	*z*
$[Ni(NH_2CH_2CH_2NHCH_2CH_2OH)_2]^{2+}$ cation			
Ni	0.2491(1)	0.1757(1)	0.1694(2)
O11	0.3190(4)	0.0506(6)	−0.1069(7)
N11	0.2732(5)	−0.0606(8)	0.1654(9)
N12	0.1850(6)	0.225(1)	0.432(1)
C11	0.3490(7)	−0.121(1)	−0.140(1)
C12	0.2798(7)	−0.176(1)	−0.031(1)
C13	0.1939(7)	−0.077(1)	0.284(1)
C14	0.1871(8)	0.070(1)	0.467(1)
O21	0.3960(4)	0.2509(6)	0.2730(7)
N21	0.2375(5)	0.4108(8)	0.1639(9)
N22	0.1089(5)	0.1568(9)	0.027(1)
C21	0.4031(7)	0.422(1)	0.308(1)
C22	0.3397(6)	0.463(1)	0.162(1)
C23	0.1731(7)	0.402(1)	0.001(1)
C24	0.0799(7)	0.318(1)	0.011(1)
H101	0.2592(4)	0.079(6)	−0.1714(7)
H102	0.3404(5)	−0.065(8)	0.2156(9)
H212	0.0435(7)	0.296(1)	−0.094(1)
H207	0.371(6)	0.40(1)	0.04(1)
H209	0.216(6)	0.34(1)	−0.11(1)
H203	0.067(7)	0.13(1)	0.07(1)
H204	0.112(6)	0.08(1)	−0.07(1)
H205	0.374(6)	0.48(1)	0.43(1)
H109	0.200(6)	−0.16(1)	0.29(1)
H110	0.146(7)	−0.08(1)	0.24(1)
H105	0.357(6)	−0.20(1)	−0.28(1)
H211	0.048(6)	0.38(1)	0.12(1)
H208	0.344(6)	0.57(1)	0.19(1)
H107	0.223(7)	−0.18(1)	−0.06(1)
H210	0.160(6)	0.51(1)	0.00(1)
H106	0.396(7)	−0.12(1)	−0.12(1)
H206	0.474(6)	0.44(1)	0.28(1)
H103	0.149(8)	0.26(1)	0.44(1)
H111	0.130(6)	0.06(1)	0.53(1)
H202	0.210(6)	0.47(1)	0.27(1)
H108	0.298(6)	−0.26(1)	−0.05(1)
H104	0.214(6)	0.30(1)	0.50(1)
H112	0.249(7)	0.06(1)	0.51(1)
Nitrate anions			
N31	0.4838(6)	0.2002(9)	0.6652(9)
O31	0.4959(5)	0.1600(9)	0.8031(8)
O32	0.5534(7)	0.1800(9)	0.556(1)
O33	0.3983(5)	0.262(1)	0.647(1)
N41	0.0922(6)	−0.2882(9)	−0.437(1)
O41	0.0566(5)	−0.1663(8)	−0.3016(9)
O42	0.1792(6)	−0.353(1)	−0.440(1)
O43	0.0434(6)	−0.344(1)	0.581(1)

stabilisation, as when an oxygen donor is added to acetate to give hydroxyacetate, the increase in steric strain is low enough that bonding effects predominate, and we observe greater stabilisation for the complex of the small Cu^{II} ion on addition of a neutral oxygen donor than for the larger metal ions such as Pb(II). However, for larger more sterically demanding ligands the electronic bonding effects are outweighed by steric effects, and the usual order where the complexes of large metal ions are stabilized more than those of small by addition of neutral oxygen donors is observed.

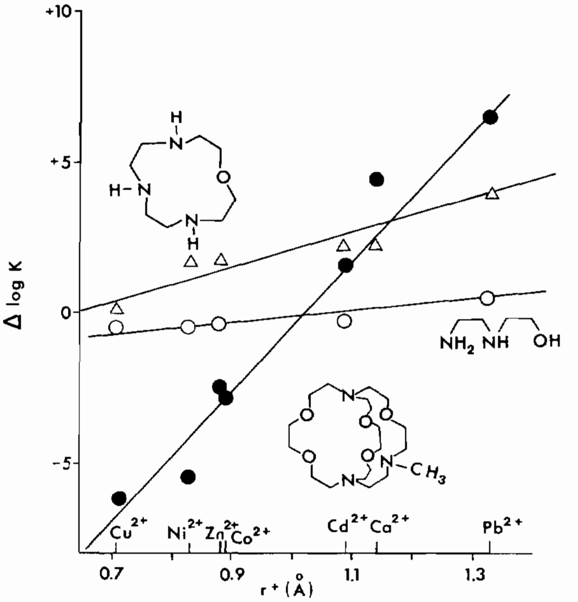


Fig. 2. Change in complex stability, Δlog *K*, as a function of metal ionic radius [10] on adding groups bearing neutral alcoholic or ethereal donors to existing amine ligands. The steepest relationship (●) is for the difference in complex stability between DIEN (L_{11}) and L_{13}, also shown on the diagram. The next relationship (△) is for passing from DIEN to L_{12}, and the shallowest (○) is for Δlog *K* between L_1 and L_5. The steepness of the slope for each relationship is an indication of how well the structural change made can produce size-selectivity for metal ions. Formation constant data are from ref. 21, except for Ce^{2+} with L_{12} which is from ref. 22.

It might seem odd to some readers to include both transition metal ions such as Cu^{2+} and Ni^{2+} in the same correlation, involving size alone as a consideration, with ionically bound metal ions such as Ca^{2+} or Pb^{2+}. However, in a recent analysis of Lewis acid–base behaviour in aqueous solution [11] it appeared that bonding differences between transition and non-transition metal ions were best regarded as differences in degree rather than kind. One might also balk at examining the complexing properties of a ligand such as L_{13} in relation to those of L_{11}. All the donor atoms of the potentially octadentate L_{13} cannot be coordinated to the Cu^{II}, which, with its expected Jahn–Teller distortion should have a rather complex structure, whereas in the complex with L_{11} all the donor atoms can be coordinated, and a rather simple structure is expected. The answer to this is that dozens of relationships of the kind seen in Fig. 2 can be drawn up, and their linearity suggests that this is a useful way to approach the

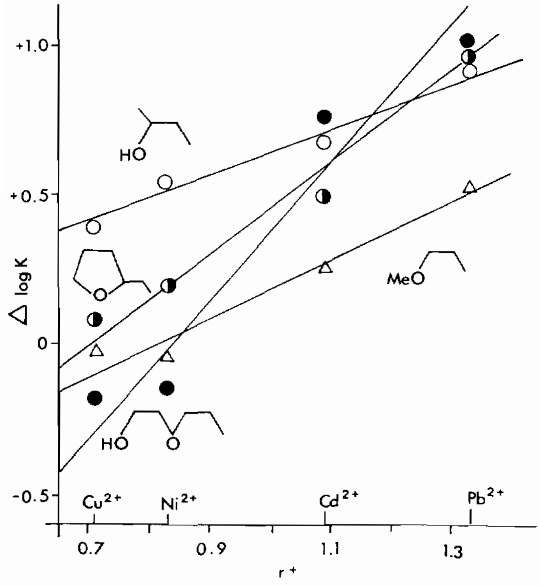


Fig. 3. Change in complex stability, Δlog *K*, as a function of metal ionic radius [10] on adding groups bearing neutral alcoholic or ethereal donors to di-2-hydroxypropylamine to give the substituted amines L_7 to L_{10}. The steepness of each slope is an indication of how well each type of oxygen donor bearing group can produce size-selectivity. Ligands are: L_7 (○), L_8 (△), L_9 (◑), L_{10} (●).

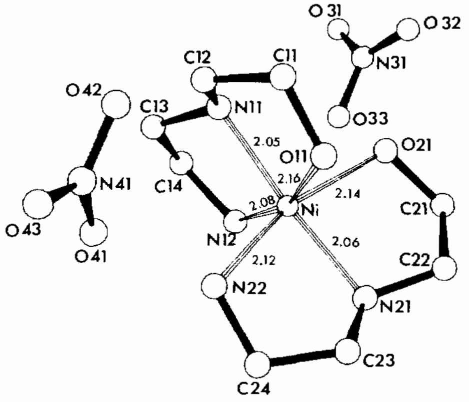


Fig. 4 ORTEP diagram of the $[Ni(NH_2CH_2CH_2NHCH_2CH_2OH)_2]^{2+}$ cation showing the numbering scheme. The bond lengths to nickel are shown, indicating the rather long Ni–O bond. Bond lengths in Å. The thermal ellipsoids are drawn at the 50% probability level. The rather large thermal ellipsoids for the nitrates appear to be caused by disorder.

problem of the relationship between structure and stability in complexes of mixed donor ligand containing both nitrogen and alcoholic or ethereal oxygen donors.

In Fig. 3 are seen similar relationships, with Δlog *K* being calculated for the complexes of L_7 to L_{10} relative to L_6. We are thus in all cases examining the size-dependence of the stability change produced by adding a neutral oxygen-donor bearing group in place of the N–H hydrogen atom of L_6. We see that the slopes of these relationships decrease in the order $L_{10} > L_9 > L_8 > L_7$. It is not surprising that L_{10} produces greater metal ion size selectivity, since it has one more oxygen donor atom, and so need not be discussed further here. What is of interest is that the THF group of L_9 produces considerably sharper metal ion size selectivity than does the 2-hydroxypropyl group of L_7 or the methoxyethyl group of L_8. This must relate to the greater rigidity of the group than the groups on L_7 or L_8, and suggests that its occurrence in L_4, and also antibiotics such as nonactin, L_{14}, might relate to this sharper size selectivity. This type of information is also of importance to us in our current program of design of ligands for the complexation of large toxic metal ions such as Cd^{2+}, Pb^{2+}, and Hg^{2+}. Thus, a ligand such as L_{15} which appears to be highly promising for treating lead poisoning does not appear to have quite the desired lead/zinc selectivity for use in living systems, but could be made more selective for the large Pb^{2+} ion by modification to give L_{16}.

The neutral oxygen donor in alcohols and ethers is analogous to the donor atom of water, and they might be thought to be exactly equivalent as donor atoms. Much work on gas-phase basicity [12] has shown that in fact the base strength increases strongly along the series $H_2O < ROH < R_2O$, where R is an alkyl group such as methyl or ethyl. We might thus expect [4] that neutral alcoholic or ethereal oxygen donors would be better donors than water, and that chelating groups bearing alcoholic or ethereal groups would lead to increases in complex stability for all metal ions. This expectation is born out for large metal ions such as Pb^{2+}, La^{3+}, or Ca^{2+}, but not for small metal ions such as Cu^{2+} or Zn^{2+}, where complex stability decreases. As suggested in the introduction, this could reasonably be due to steric crowding in small metal ions, and we here examine this question by examining the crystal structure of $[Ni(L_5)_2](NO_3)_2$ (Fig. 4). The structure of the $[Ni(L_5)]^{2+}$ cation is similar to that reported [13] for the $[Ni(L_{11})_2]^{2+}$ cation, with meridional coordination of the ligands. What is of interest is the rather long Ni–O bond lengths which average 2.15 Å. These are very much longer than found for the Ni–O bond lengths to coordinated water molecules in complexes of high-spin Ni(II). Thus, the Ni–O bond lengths in $[NiL_1(H_2O)_4]^{2+}$ are 2.09 Å [14], in $[Ni(L_1)_2(H_2O)_2]^{2+}$ are 2.10 Å [15], and in $[Ni(H_2O)_6]^{2+}$ itself are 2.06 Å [16]. One could argue here that this is a steric effect, or else that alcohols are intrinsically weaker donors with naturally longer Ni–O bonds. In order to answer this type of question, we are currently developing a molecular mechanics force field for mixed oxygen and nitrogen donors [17]. This force field does not differentiate between oxygen in water or alcoholic groups, *i.e.* both types of oxygen are modelled with the same force constants and strain-free bond lengths and angles. It is able to reproduce the above set of Ni–O bond lengths very satisfactorily, predicting, for example, Ni–O bond lengths of 2.06 Å in $[Ni(H_2O)_6]^{2+}$, 2.09 in $[NiL_1(H_2O)_4]^{2+}$, and 2.17 Å in $[Ni(L_5)_2]^{2+}$. The origin of the Ni–O bond stretching in the latter complex is Van de Waals repulsive interactions between the hydrogens on the ethylene bridges of the ligand. Similar steric interactions are present [18] in the analogous complex with L_{11}. Here, however, the nitrogen donor is with most metal ions (Cu^{2+} or Zn^{2+}, for example, but not Ca^{2+}) a stronger donor than oxygen. There is thus little chance that the steric strain induced on adding an aminoethyl group to L_1 to give L_5 will lead to an overall decrease in stability, since the added amine group binds much more strongly than does the displaced water. The effect of the greater strain in the DIEN ring (L_{11}) than of the EN (L_1) ring is seen [19] in that, for example, ΔH of complex formation is -105.9 kJ mol^{-1} for $[Ni(L_{11})_2]^{2+}$, whereas it is -117.2 kJ mol^{-1} for $[Ni(L_1)_3]^{2+}$. To sum up these observations, the strain energy in complexes of L_5 is probably quite similar to that in complexes of L_{11}. However, the base strength of the alcoholic oxygen in L_5 is for most metal ions much less than the amine group in its place in L_{11}. In the balance between induced steric strain and extra base strength in adding an extra chelate ring to L_1, the balance with small metal ions tips in favour of steric strain when we add an alcoholic group to give L_5, and so a nett drop in stability results. This steric strain is manifest in the long Ni–O bond of 2.15 Å in $[Ni(L_5)_2]^{2+}$ as compared with 2.10 Å in $[Ni(L_1)_2(H_2O)_2]^{2+}$. In large metal ions such as Ca^{2+} or Pb^{2+}, this steric strain will be less, and the greater basicity of the alcoholic oxygen relative to water should predominate.

Supplementary Material

Thermal parameters are observed and calculated structure factors are available as supplementary material.

Acknowledgements

We thank the Council Research Grants Committee of the University of the Witwatersrand, and the Foundation of Research Development for generous financial support.

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