Exomacrocyclic Complexation: The Speciation of Copper(II) and Nickel(II) Complexes of the Dibenzo-pyrido-macrocycle 3,22-Dioxa-11,14,28-triazatetracyclo-[22.3.1.$0^{4,9}$,$0^{16,21}$]octacosa-1(28),4,6,8,16,18,20,24,26-nonaene

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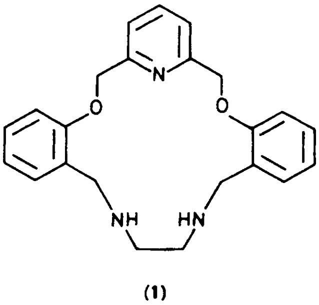
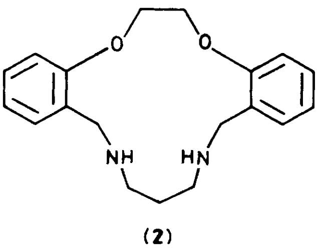
Speciation studies of copper(II) and nickel(II) complexes of the title macrocycle in dimethyl sulphoxide reveal the presence of 1 : 1 and 1 : 2 metal : ligand ratios; the crystal structures of the 1 : 1 copper(II) perchlorate and the 1 : 2 nickel(II) nitrate complexes are reported.

Aspects of ligand design which lead to high selectivity of metal complex formation are of relevance to areas ranging from biochemistry to hydrometallurgy. The most useful systems for selective complexation and the transport of metal ions are those with intermediate rigidity, sufficient to present a donor set with a defined geometry, but flexible enough to give favourable kinetics of complex formation and decomposition.[1] For systems of this type, good discrimination depends on incorporation of the metal ion into the donor cavity of the ligand to form a 1:1 complex, and stability constants have been found to correlate well with the goodness-of-fit for the donor cavity.[2] When metal ions are discriminated against by a poor fit for the cavity the probability exists that the most favourable mode of interaction will involve exocyclic complexation using only part of the macrocyclic donor set.[3]



(1)



(2)

It is of value to understand the speciation in any reaction between a metal ion and a macrocycle and also in a multicomponent system to be aware of the nature of the species present. We have found, in an investigation of the reactions between the title dioxa-triazamacrocycle (**1**), with copper(II) and nickel(II) salts, that it has been possible to make a close correlation between the species available in solution and in the solid state.

Spectrophotometric titrations of (**1**) with the metal perchlorate in dimethyl sulphoxide (dmso) are consistent with the

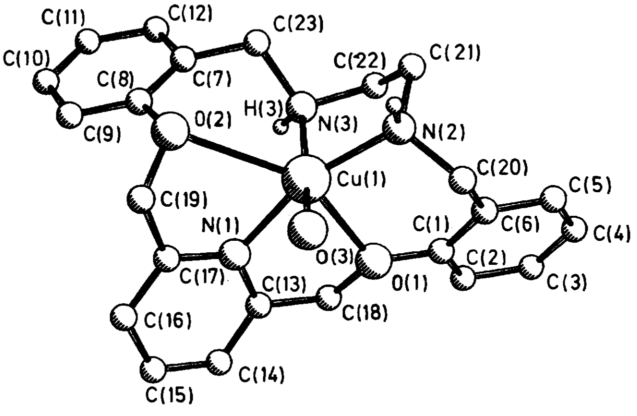


Figure 1. The molecular geometry of the complex cation $[Cu(\mathbf{1})H_2O]^{2+}$.

Table 1. The co-ordination environment of the metal ion.

(a) The copper complex

	Bond length/Å	Bond angles/°				
Cu O(1)	2.30(4)					
Cu O(2)	2.67(3)	145.4(1)				
Cu O(3)	2.02(5)	97.6(2)	90.4(2)			
Cu N(1)	2.02(5)	76.1(2)	70.6(2)	87.8(2)		
Cu N(2)	1.99(5)	88.7(2)	125.4(2)	86.8(2)	163.1(2)	
Cu (N3)	2.03(5)	98.2(2)	81.5(2)	161.9(2)	104.5(2)	84.8(2)
		O(1)	O(2)	O(3)	N(1)	N(2)

(b) The nickel complex

Ni O(4)	2.21(2)					
Ni O(4ª)	2.21(2)	58.5(12)				
Ni N(2)	2.14(2)	92.2(8)	99.5(8)			
Ni N(3)	2.15(3)	94.0(9)	152.5(9)	81.4(8)		
Ni N(2ª)	2.14(2)	99.5(8)	92.2(8)	166.6(12)	91.3(8)	
Ni N(3ª)	2.15(3)	152.5(9)	94.0(9)	91.3(8)	113.5(14)	81.4(8)
		O(4)	O(4ª)	N(2)	N(3)	N(2ª)

formation initially of a species with a 1 : 1 metal : ligand ratio [λ_{max} = 650 nm (ε = 150) (Cu); 660 (3.7), 388 nm (17) (Ni)] followed by the formation of a 1 : 2 species [λ_{max} = 606 nm (ε = 133) (Cu); 622 (5.8), 378 nm (22) (Ni)]. The relative positions of the bands are indicative of octahedral complexes and the shift to higher energy noted for the 1 : 2 species suggests a larger nitrogen donor contribution to the donor set for that species. A similar solution behaviour has been reported for the interaction of the related dioxa-diazamacrocycle (**2**) with copper(II) in solution;[4] however in the present study crystals of both species have been obtained from methanolic solutions and the structures solved for the complexes Cu(**1**) $(ClO_4)_2$, H_2O and Ni (**1**)$_2$ $(NO_3)_2$, 2MeOH.

The crystal structure of the[†] copper(II) complex shows the metal to be in a six co-ordinated restricted tetragonal rhombic environment provided by the five macrocyclic donor atoms and a water molecule (Figure 1; Table 1a). It is likely that in dmso solution the water molecule is replaced by a solvent molecule and that the overall co-ordination geometry is retained. The structure of the 1 : 2 complex of nickel(II) shows the metal to be again six co-ordinated the environment being provided by the aliphatic nitrogen atoms from the macrocycle, one pair from each ring, and a bidentate nitrate anion; the nickel(II) is therefore complexed in an exomacrocyclic manner (Figure 2; Table 1b). The distortion from octahedral geometry may be associated with the different ligand bites provided by the nitrate anion and the diamino-bridge from the macrocycle. It is noted that the configuration of these aliphatic nitrogen atoms is *RR* in the copper complex and *RS* in the nickel complex. On dissolution it is likely that the anion is replaced by two solvent molecules to maintain the co-ordination environment. Although the exomacrocyclic complexation of a metal by a macrocycle has been noted,[3] the above structure represents, to our knowledge, the first example for a 1 : 2 complex from the interaction of transition metal ions with Schiff's base derived oxa-azamacrocycles.

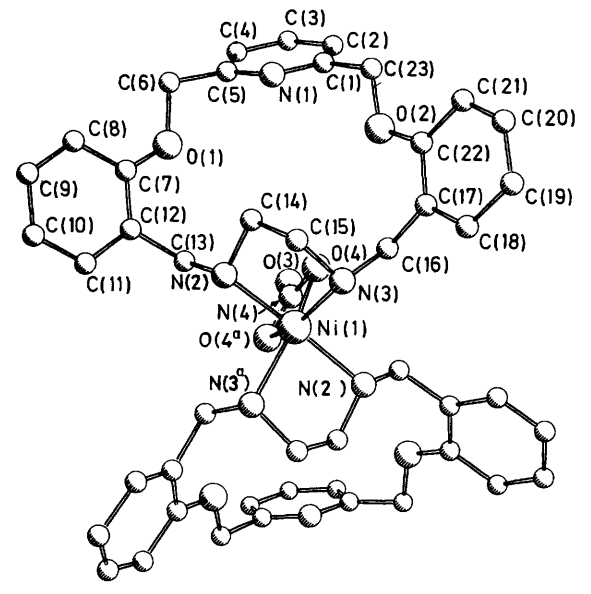


Figure 2. The molecular geometry of the complex cation $[Ni(\mathbf{1})_2(NO_3)]^+$.

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[†] *Crystal data*: $[Cu(\mathbf{1})(ClO_4)_2, H_2O]$ $C_{23}H_{27}Cl_2N_3O_{11}Cu$, M = 655.5, monoclinic, space group $P2_1/n$ [non-standard setting of $P2_1/c$ (C_{2h}^5, No. 14)], a = 12.350(27), b = 13.879(16), c = 15.954(30) Å, β = 101.16(16)^0, Z = 4, U = 2682(8) Å^3, D_c = 1.624 g cm^{-3}, μ(Mo-K_α) = 10.78 cm^{-1}, R = 0.0603 for 3266 reflections [$|F|/\sigma(|F|) > 3.0$], collected on a Nicolet R3 diffractometer.

$[Ni(\mathbf{1})_2(NO_3)_2, 2CH_3OH]$ $C_{48}H_{58}N_8O_{12}Ni$, M = 997.7, monoclinic, space group $C2/c$ (C_{2h}^6, No. 15), a = 19.665(29), b = 14.449(28), c = 18.335(19) Å, β = 108.44(9)°, Z = 4, U = 4942(13) Å^3, D_C = 1.341 g cm^{-3}, μ(Mo-K_α) = 4.58 cm^{-1}, R = 0.1655 for 1388 reflections of moderate quality [$|F|/\sigma(|F|) > 3.0$], collected on a Nicolet R3 diffractometer.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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