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X-ray crystal structures of the copper(II), nickel(II) and silver(I) complexes of a 17-membered dibenzo macrocycle with a N_3S_2 donor set

Uwe Kallert and **Rainer Mattes***
Institute of Inorganic Chemistry, Westfälische Wilhelms-Universität, Wilhelm-Klemm-Strasse 8, 4400 Münster (F.R.G.)

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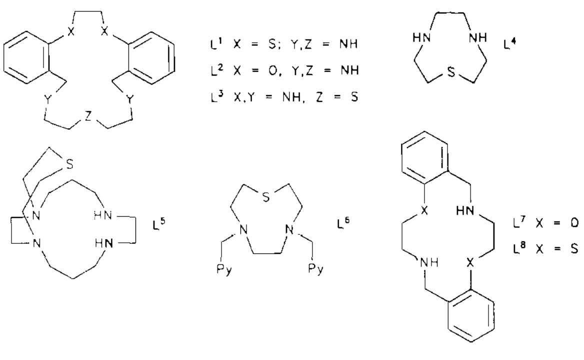
Abstract

The copper(II), nickel(II) and silver(I) complexes of the pentadentate 17-membered macrocycle 1,12,15-triaza-3,4:9,10-dibenzo-5,8-dithiacycloheptadecane (L^1) have been prepared as perchlorates and characterized by X-ray crystallography. The N_3S_2 ligand uses all donor atoms for complexation. The copper coordination is square pyramidal with one sulfur atom in the axial site. Ni(II) displays an octahedral coordination by an interaction with a water molecule. The Ag(I) coordination is best described as a distorted pentagonal bipyramid. In $[CuL^1]^{2+}$ the 1,4,7-triazaheptane fragment of L^1 is meridionally coordinated, but facially in $[NiL^1(H_2O)]^{2+}$ and intermediate in $[AgL^1](ClO_4)$. Crystal data for $[CuL^1](ClO_4)_2$: monoclinic, space group $P2_1/n$, $a = 13.153(8)$, $b = 11.951(5)$, $c = 17.880(8)$ Å, $\beta = 110.29(4)°$, $Z = 4$, $R = 0.086$ for 2732 independent reflections with $I \geqslant 2\sigma(I)$; $[NiL^1(H_2O)](ClO_4)_2$: monoclinic, $P2_1/a$, $a = 10.771(2)$, $b = 16.157(2)$, $c = 15.286(2)$ Å, $\beta = 93.08(1)°$, $Z = 4$, $R = 0.085$ for 1464 independent reflections with $I \geqslant 2\sigma(I)$; $[AgL^1](ClO_4)$: monoclinic, $P2_1/n$, $a = 12.708(9)$, $b = 9.483(7)$, $c = 19.569(13)$ Å, $\beta = 103.95(6)°$, $Z = 4$, $R = 0.039$ for 3600 independent reflections with $I \geqslant 2\sigma(I)$.

Introduction

The metal ion chemistry of synthetic macrocycles is of fundamental importance in chemistry and biochemistry. The development of macrocyclic systems of potential use for metal ion discrimination and the understanding of the mechanisms of such recognition has been extensively studied in the last few years [1a]. Macrocylic and chelate ring size [1b], nature of the donor atoms, and the coordination properties of the metal ions mainly determine the structure and the thermodynamic stabilities of their complexes. We have investigated in a number of studies the binding preferences of the mixed donor atom nine-membered macrocycle 1-thia-4,7-diazacyclononane (L^4, see Scheme 1) [2]. This small macrocyclic ligand usually coordinates facially to a metal ion or atom. Exceptions are $[Pt(L^4)_2]^{2+}$, where only the N_2 donor set is used for complexation, and $[AgL^4]^+$, which forms S-bridged cyclic tetrameres [2].



Scheme 1. Ligands referred to in the text.

Recently Lindoy and coworkers [3–9] published the syntheses of an extensive series of potentially pentadentate 17-membered dibenzo macrocyclic ligands containing nitrogen, oxygen and/or sulfur atoms (e.g. L^1, L^2, L^3). Crystal structures of two of these ligands and of several complexes with N_3O_2 (L^2) and N_4S (L^3) donor sets have been presented as well. According to these studies the 1,4,7-triazaheptane macrocyclic fragment of these ligands can coordinate metal ions either in a facial or in a meridional manner. In extension to our work on the ligating properties of mixed N,S donor macrocyclic ligands we prepared the Cu(II), Ni(II) and Ag(I) complexes of the 17-membered macrocycle 1,12,15-triaza-3,4:9,10-dibenzo-5,8-dithiacycloheptadecane (L^1) with a N_3S_2 donor set. In the present paper we describe the crystal structures of these complexes. They are of particular interest since these ligands

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*Author to whom correspondence should be addressed.

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incorporate both hard and soft donor atoms in a restricted environment, but are locally flexible with respect to the coordination mode of the N_3 fragment as mentioned above. Stability constants have been obtained for the nickel(II) complexes of L^1 and L^2 [4], and for the 1:1 copper(II) complexes of the whole series of ligands [9]. They depend as expected on the donor atom sets. Accordingly, the complex $[CuL^1]^{2+}$ is approximately ten times more stable than $[CuL^3]^{2+}$. A comparison of their structural parameters and their stereochemistries may give more insight into this property. The interaction of L^1 with Ag(I) has been measured using calorimetry and ^{1}H NMR spectroscopy [10].

Experimental

Syntheses

1,12,15-Triaza-3,4:9,10-dibenzo-5,8-dithiacycloheptadecan (L^1) was prepared as described previously [8]. All starting materials were commercially available.

$[CuL^1](ClO_4)_2$

A hot ethanolic solution (10 ml) of the free ligand L^1 (0.195 g, 0.5 mmol) was added to a stirred boiling solution (20 ml) of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.185 g, 0.5 mmol) in ethanol. The solution immediately turned blue, but was heated under reflux for 2 h to ensure complete complexation. $[CuL^1](ClO_4)_2$ precipitated as the solution cooled.

Anal. Calc. for $CuC_{20}H_{27}N_3S_2Cl_2O_8$: C, 37.80; H, 4.28; N, 6.62. Found: C, 37.78; H, 4.29; N, 6.71%. Yield 0.28 g (90%). IR (KBr): NH(stretch) 3240, 3200 cm^{-1}, ClO_4 1100, 1090, 620 cm^{-1}. Dark blue crystals of X-ray quality were obtained by recrystallization from ethanol.

$[NiL^1(H_2O)](ClO_4)_2$

Deep purple crystals of this compound were prepared by a similar procedure from $Ni(ClO_4)_2 \cdot 6H_2O$.

Anal. Calc. for $NiC_{20}H_{29}N_3S_2Cl_2O_9$: C, 36.98; H, 4.47; N, 6.48. Found: C, 37.00; H, 4.28; N, 6.40%. Yield 0.19 g (60%). IR (KBr): NH(stretch) 3240, 3200 cm^{-1}, ClO_4 1100, 1090, 620 cm^{-1}.

$[AgL^1](ClO_4)$

White clear crystals of this compound were prepared by a similar procedure from $Ag(ClO_4)$.

Anal. Calc. for $AgC_{20}H_{27}N_3S_2ClO_4$: C, 41.35; H, 4.69; N, 7.23. Found: C, 40.77; H, 4.78; N, 7.09%. Yield 0.20 (69%) IR (KBr): NH(stretch) 3320, 3290 cm^{-1}; ClO_4 1100, 1090, 620 cm^{-1}.

Caution: transition-metal complex perchlorates are known to be hazardous and must be treated with care, especially in the presence of organic solvents.

TABLE 1. Crystal parameters and experimental data for X-ray diffraction measurements

	$[CuL^1](ClO_4)_2$	$[NiL^1(H_2O)](ClO_4)_2$	$[AgL^1](ClO_4)$
Chemical formula	$C_{20}H_{27}N_3S_2CuCl_2O_8$	$C_{20}H_{29}N_3S_2NiCl_2O_9$	$C_{20}H_{27}N_3S_2AgClO_4$
Molecular weight	636.0	649.2	580.4
Lattice type	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/a$	$P2_1/n$
a (Å)	13.153(8)	10.771(2)	12.708(9)
b (Å)	11.951(5)	16.157(2)	9.483(7)
c (Å)	17.880(8)	15.286(2)	19.569(13)
β (°)	110.29(4)	93.08(1)	103.95(6)
V (Å^3)	2636(2)	2656.3(5)	1192.4(5)
Z	4	4	4
$D_{calc}(D_{obs})$ (g cm^{-1})	1.60(1.64)	1.62(1.74)	1.62(1.60)
$F(000)$	1308	1344	1184
Crystal dimensions (mm)	0.15×0.2×0.2	0.1×0.1×0.1	0.25×0.15×0.2
Absorption coefficient (Mo Kα) (mm^{-1})	1.23	1.14	1.19
Absorption correction			ψ-scan
2θ range (°C)	4–54	4–54	4–48
Scan speed (°/min)	1.1–5.4	1.1–5.4	3.3–29.3
Background/scan time	0.5	0.5	0.5
Data collected	6283	5590	3979
Unique data with $I \geqslant 2\sigma(I)$	2732	1464	3600
No. variables	265	219	292
Goodness of fit	2.60	1.79	1.37
$R(R_w)$	0.086(0.082)	0.085(0.069)	0.039(0.038)
Residual density (e Å^{-3})	+0.8, −0.7	+0.6, −0.5	+1.24, −0.6

Crystallography

Diffraction studies were performed at 293 (Ni and Cu complex) and 77 (Ag complex) K with a Mo X-ray source (Kα radiation = 0.71073 Å) equipped with a graphite monochromator. Intensities were collected by using the $\varpi/2\theta$ scan mode. The final orientation matrix and unit cell parameters were determined by least-squares treatment of 25 machine-centered reflections having $2\theta > 19°$ for $[CuL^1](ClO_4)_2$, 18 reflections having $2\theta > 13°$ for $[NiL^1(H_2O)](ClO_4)_2$ and 15 reflections having $2\theta > 16°$ for $[AgL^1](ClO_4)$. For $[CuL^1](ClO_4)_2$ the intensities of three check reflections (-3 -5 0, -6 0 0, 0 0 10) showed 5% decay during data acquisition. No variation was observed for the two check reflections of $[NiL^1(H_2O)](ClO_4)_2$ and $[AgL^1](ClO_4)$. Check reflections were measured every 2 h. Crystal data are given in Table 1. No absorption corrections were applied for two compounds because of the small absorption coefficients, the size and the isometric shape of the crystals.

Structure solution and refinement

The structures were solved by direct methods and refined by standard least-squares methods using the SHELXTL PLUS [11] program system. Aromatic carbon atoms were refined isotropically for $[CuL^1](ClO_4)_2$ and $[NiL^1(H_2O)](ClO_4)_2$, for the latter aliphatic carbons as well. The remaining non-hydrogen atoms were refined with anisotropic thermal parameters. For $[AgL^1](ClO_4)$ all non-hydrogen atoms were refined anisotropically. C–H, N–H and CH_2 groups were refined as rigid moieties with fixed isotropic thermal parameters for the hydrogen atoms ($U_H = 0.08$ Å^2). The weighting scheme $w^{-1} = \sigma(F)^2 + 0.0004F^2$ was used throughout. Final R factors are included in Table 1. Atom positional parameters and selected bond lengths and angles are given in Tables 2–5.

Views of the cations $[CuL^1]^{2+}$, $[NiL^1(H_2O)]^{2+}$ and $[AgL^1]^+$ with atom labelling schemes are given in Figs. 1, 2 and 3, respectively.

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for $[CuL^1](ClO_4)_2$

	x	y	z	U_{eq}[a]
Cu	3587(1)	1174(1)	1412(1)	51(1)
S(1)	5062(2)	1438(2)	2594(1)	59(1)
S(2)	4939(2)	1666(2)	698(1)	56(1)
Cl(1)	2045(4)	633(4)	−1597(2)	120(2)
Cl(2)	2412(4)	1594(3)	3079(2)	105(2)
N(1)	3637(7)	−504(6)	1529(4)	58(4)
N(2)	2193(8)	919(8)	503(5)	75(4)
N(3)	3035(7)	2751(7)	1354(4)	55(4)
O(11)	1700(13)	1485(11)	8751(6)	180(9)
O(12)	2331(18)	996(13)	7753(7)	238(13)
O(13)	2940(14)	224(14)	8969(6)	218(10)
O(14)	1350(18)	−86(27)	8141(16)	365(20)
O(21)	2576(9)	799(7)	2566(6)	114(5)
O(22)	2396(8)	2664(7)	2784(5)	104(5)
O(23)	1505(15)	1416(10)	3264(13)	244(15)
O(24)	3206(18)	1507(15)	3793(7)	258(13)
C(1)	4726(10)	−1031(9)	1864(6)	68(5)
C(2)	5177(8)	−872(9)	2750(6)	62(3)
C(3)	5274(9)	145(9)	3138(6)	60(3)
C(4)	5469(10)	−1852(11)	3216(7)	87(4)
C(5)	5834(10)	−1673(11)	4053(7)	85(4)
C(6)	5853(10)	−692(11)	4395(8)	87(4)
C(7)	5599(9)	256(10)	3931(6)	71(3)
C(8)	6248(9)	1462(9)	2303(6)	70(5)
C(9)	6072(8)	2169(9)	1549(6)	64(5)
C(10)	4382(7)	2931(8)	197(5)	47(2)
C(11)	3916(8)	3742(8)	513(5)	50(2)
C(12)	4418(9)	3062(9)	−543(6)	66(3)
C(13)	3984(9)	4005(10)	−1002(7)	74(3)
C(14)	3539(9)	4788(10)	−717(7)	71(3)
C(15)	3519(8)	4696(9)	32(6)	63(3)
C(16)	3772(9)	3689(8)	1304(5)	57(4)
C(17)	1957(9)	2829(10)	739(7)	75(6)
C(18)	1399(9)	1713(11)	608(7)	81(6)
C(19)	1923(13)	−299(12)	476(7)	109(8)
C(20)	2990(12)	−932(10)	712(7)	86(6)

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor. U_{iso} is given for C(2) to C(7) and C(10) to C(15).

Results and discussion

$[CuL^1](ClO_4)_2$, $[NiL^1(H_2O)](ClO_4)_2$ and $[AgL^1](ClO_4)$ were readily prepared by addition of L^1 to the corresponding metal perchlorate solution in hot ethanol. The 1:1 stoichiometry was confirmed by microanalysis. The infrared spectrum of $[CuL^1](ClO_4)_2$ showed splitting of the perchlorate ν^3 bond, consistent with weak coordination of the anion in solid state. In all three complexes the N_3S_2 ligand uses all donor atoms for complexation.

The coordination of copper(II) is best described as square pyramidal $Cu(N_3S)S$ with the copper atom lying out of the N_3S plane, 0.234 Å towards the second S donor. Copper weakly interacts with a perchlorate ion (Cu···O = 2.28 Å). The Cu–N bond lengths are nearly equal (2.00, 2.01 Å) but rather short. Slightly longer bonding distances of amine nitrogen atoms have been observed recently in three copper complexes with N_4S donor sets, e.g. $[CuL^3](ClO_4)_2$ [9] $[CuL^5](ClO_4)_2$ [12] and $[CuL^6](ClO_4)_2$ [13] with mean values between 2.04 and 2.05 Å. The N–Cu–N angles are 83.6(4), 85.4(4) and 160.0(4)°. Due to the restricted ligand bite N(1)···N(3), the last value is untypical for *trans*-basal angles of square-pyramidal d^9 Cu(II) complexes

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[NiL^1(H_2O)](ClO_4)_2$

	x	y	z	U_{eq}
Ni	2365(2)	−27(2)	2206(1)	46(1)
S(1)	1915(5)	−615(3)	3593(3)	56(2)
S(2)	3130(4)	−1402(3)	1887(3)	52(2)
Cl(1)	−1694(6)	1075(4)	724(3)	66(2)
Cl(2)	223(6)	6708(4)	5340(4)	70(2)
O(1)	654(10)	−566(7)	1549(7)	64(5)
O(11)	3612(16)	4017(17)	1556(10)	212(14)
O(12)	3698(26)	4662(13)	437(16)	230(16)
O(13)	2112(16)	3820(16)	524(12)	207(14)
O(14)	4056(17)	3436(14)	296(15)	207(13)
O(21)	4616(23)	885(10)	4676(11)	197(13)
O(22)	4325(30)	2052(15)	5294(20)	291(20)
O(23)	4311(26)	1963(12)	3890(14)	248(16)
O(24)	5907(23)	1929(19)	4716(24)	309(22)
N(1)	1312(12)	1006(8)	2469(8)	56(4)
N(2)	2819(13)	643(9)	1104(8)	56(4)
N(3)	4123(11)	379(7)	2671(8)	46(4)
C(1)	1005(17)	1148(11)	3407(11)	71(6)
C(2)	108(17)	510(12)	3694(10)	56(5)
C(3)	367(17)	−281(11)	3791(11)	59(6)
C(4)	−1117(18)	812(14)	3888(11)	82(7)
C(5)	−1951(17)	214(11)	4177(10)	67(6)
C(6)	−1652(19)	−585(13)	4233(11)	78(6)
C(7)	−485(18)	−886(12)	4035(11)	72(6)
C(8)	1800(16)	−1683(11)	3325(12)	71(6)
C(9)	2975(15)	−1943(11)	2931(10)	71(6)
C(10)	4765(15)	−1378(10)	1801(10)	49(5)
C(11)	5527(16)	−826(10)	2272(10)	41(4)
C(12)	5282(15)	−1870(10)	1167(10)	48(5)
C(13)	6494(16)	−1838(11)	1041(11)	61(5)
C(14)	7267(17)	−1310(10)	1487(10)	57(5)
C(15)	6784(16)	−783(11)	2121(10)	59(50
C(16)	5011(15)	−274(9)	2989(10)	55(5)
C(17)	4694(16)	898(11)	2019(10)	65(6)
C(18)	4176(15)	705(11)	1087(10)	56(5)
C(19)	2163(18)	1458(12)	1126(12)	86(7)
C(20)	1876(17)	1722(12)	2014(11)	79(6)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor. U_{iso} is given for all carbon atoms.

TABLE 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[AgL^1](ClO_4)$

	x	y	z	U_{eq}[a]
Ag	1979(1)	2332(1)	3606(1)	31(1)
S(1)	415(1)	3167(2)	2482(1)	30(1)
S(2)	2385(1)	475(2)	2688(1)	29(1)
Cl	1840(1)	986(2)	9812(1)	35(1)
O(1)	1062(4)	714(5)	9169(2)	69(2)
O(2)	1396(4)	505(5)	10371(2)	65(2)
O(3)	2803(4)	248(6)	9813(3)	81(2)
O(4)	2053(4)	2458(4)	9894(2)	56(2)
N(1)	683(4)	3101(6)	4238(3)	36(2)
N(2)	2287(4)	837(6)	4702(3)	41(2)
N(3)	3873(3)	2402(5)	4072(2)	30(2)
C(1)	−381(4)	3588(6)	3814(3)	40(2)
C(2)	−957(4)	2474(6)	3309(3)	31(2)
C(3)	−685(4)	2189(5)	2673(3)	27(2)
C(4)	−1827(4)	1721(7)	3461(3)	42(2)
C(5)	−2404(4)	747(7)	2995(3)	43(2)
C(6)	−2143(4)	523(6)	2366(3)	40(2)
C(7)	−1295(4)	1241(6)	2192(3)	34(2)
C(8)	790(4)	2171(6)	1793(3)	33(2)
C(9)	1208(4)	669(6)	1969(3)	30(2)
C(10)	3415(4)	1438(6)	2411(3)	28(2)
C(11)	4335(4)	1842(6)	2924(3)	31(2)
C(12)	3347(4)	1738(6)	1706(3)	35(2)
C(13)	4186(4)	2451(6)	1507(3)	39(2)
C(14)	5098(4)	2853(7)	2003(3)	42(2)
C(15)	5166(4)	2546(6)	2705(3)	39(2)
C(16)	4473(4)	1452(6)	3690(3)	36(2)
C(17)	4054(5)	2065(6)	4828(3)	39(2)
C(18)	3477(5)	729(7)	4967(3)	49(2)
C(19)	1740(5)	1598(8)	5173(3)	55(3)
C(20)	610(5)	2047(8)	4762(3)	55(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

[14]. The equatorial Cu–S distance (2.346(3) Å) is comparable with literature data [15–17]. The axial Cu–S distance is 2.590(4) Å. In macrocyclic complexes with the $Cu(N_4)S$ core, like $[CuL^3]^{2+}$ (2.525(4) Å) [9], $[CuL^5]^{2+}$ (2.549(2) Å) [12] and $[CuL^6]^{2+}$ (2.496(8) Å) [13] this bond is expected to be shorter. This is indeed observed.

In $[NiL^1(H_2O)](ClO_4)_2$ the 1,4,7-triazaheptane fragment of the ligand is facially coordinated in contrast to $[CuL^1](ClO_4)_2$. A strong interaction with a coordinated water molecule (Ni$\cdots$O = 2.228(1) Å) *trans* to N(3) essentially gives a pseudooctahedral geometry. As a consequence, the nickel atom is only slightly displaced (0.065 Å) out of the equatorial N_2S_2 plane towards the axial N donor. The Ni–N bond lengths (mean 2.08(1) Å) are close to the values found in related high spin mixed donor macrocyclic complexes like $[NiL^5]^{2+}$ [12] or $[NiL^3(H_2O)]$ [5] with mean Ni–N distances of 2.06 and 2.07 Å, respectively. All the values just mentioned are shorter than the 'standard' value of 2.11 Å [18]. The two *cis*-positioned Ni–S bonds (2.396(5) and 2.428(5) Å) are slightly longer than those in homoleptic nickel(II) thioether complexes [12, 14, 19]. A similar bond distance (2.418 Å) was observed in the mixed donor complex $[Ni(L^4)_2]^{2+}$ [20]. Obviously Ni(II) prefers in mixed N,S donor complexes the hard donor atoms.

It is interesting to compare the structures of $[NiL^2(H_2O)](ClO_4)_2$ and $[NiL^1(H_2O)](ClO_4)_2$. Both are complexes of pentadentate 17-membered macrocyclic ligands, which contain the 1,4,7-triazaheptane moiety but differ in the final two donor atoms. In $[NiL^1(H_2O)](ClO_4)_2$ the metal–ligand bond dis-

TABLE 5. Selected bond lengths and angles

	M		
	Cu	Ni	Ag
Bond lengths (Å)			
M-S(1)	2.343(3)	2.396(5)	2.713(2)
M-S(2)	2.590(4)	2.428(5)	2.652(3)
M-N(1)	2.015(8)	2.070(13)	2.392(6)
M-N(2)	2.007(8)	2.083(13)	2.522(6)
M-N(3)	2.009(8)	2.092(12)	2.367(5)
M-O(1)		2.228(11)	
M-O(21)	2.851(13)		
S(1)-C(3)	1.796(11)	1.793(19)	1.788(6)
S(1)-C(8)	1.807(13)	1.776(18)	1.800(6)
S(2)-C(9)	1.823(9)	1.835(17)	1.806(5)
S(2)-C(10)	1.780(9)	1.774(17)	1.782(6)
Bond angles (°C)			
S(1)-M-S(2)	85.3(1)	84.4(2)	82.3(1)
S(1)-M-N(1)	93.0(2)	90.5(4)	82.4(1)
S(1)-M-N(2)	171.6(3)	171.6(4)	145.0(1)
S(1)-M-N(3)	95.2(2)	92.7(4)	142.1(1)
S(1)-M-O(1)		92.4(3)	
S(2)-M-N(1)	105.9(3)	166.5(4)	145.0(1)
S(2)-M-N(2)	103.1(3)	102.5(4)	100.8(1)
S(2)-M-N(3)	93.4(3)	92.6(4)	86.4(1)
S(2)-M-O(1)		80.4(3)	
N(1)-M-N(2)	85.5(3)	83.8(5)	73.8(2)
N(1)-M-N(3)	159.5(4)	101.1(5)	123.6(2)
N(1)-M-O(1)		87.4(5)	
N(2)-M-N(3)	83.6(3)	82.2(5)	75.4(2)
N(2)-M-O(1)		93.6(5)	
N(3)-M-O(1)		170.9(5)	

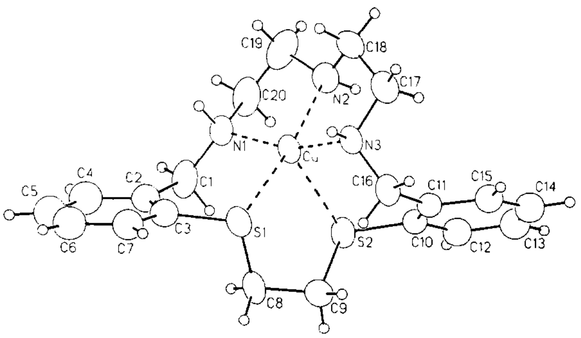

Fig. 1. Perspective view of the cation $[CuL^1]^{2+}$ and atom labelling scheme.

tances are generally closer to the standard values, whereas in $[NiL^2(H_2O)](ClO_4)_2$ with overall mirror symmetry of the complex ion rather long Ni–O bonds (2.331 and 2.125 Å) have been observed. Obviously the binding cavity of the N_3O_2 ligand L^2, even if it is folded, is too large to accommodate high spin Ni(II) ions properly. The bonding cavity of the N_3S_2 ligand L^1 seems to be smaller and therefore exhibits a much better fit for Ni(II). A related situation has been recently documented for the binding cavity sizes of the 14-membered *trans*-N_2S_2 and *trans*-N_2O_2 ligands L^7 and L^8 [21].

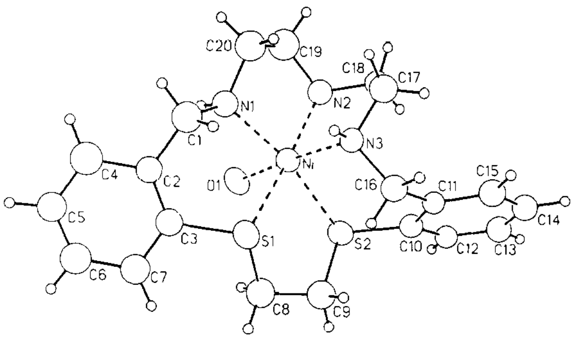

Fig. 2. Perspective view of the cation $[NiL^1(H_2O)]^{2+}$ and atom labelling scheme.

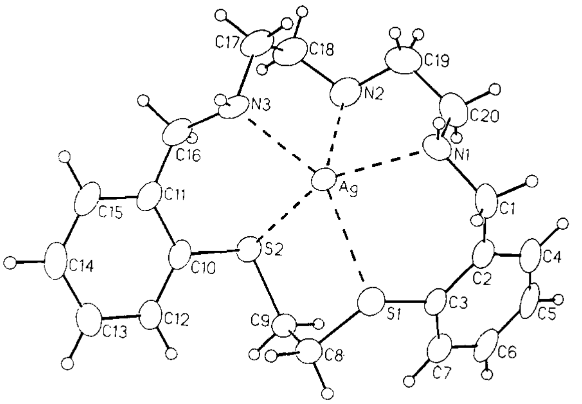

Fig. 3. Perspective view of the cation $[AgL^1]^+$ and atom labelling scheme.

The structural differences are not correlated with the stability constants determined by Lindoy (log $K = 9.9$ and 9.96, respectively). We would expect greater stability for $[NiL^1(H_2O)]^{2+}$. But the effects on log *K*, originating from the different conformations of the ligands and from the different donor sets may be opposed.

In $[AgL^1](ClO_4)$ the central ion is also coordinated by all five donor atoms (see Fig. 3). The coordination polyhedron is best described as a heavily distorted pentagonal bipyramid with N(1), N(3) and S(2) in the equatorial plane. Ag(I) is lying out of it 0.29 Å towards S(1). The Ag–S distances are 2.652(3) (Ag–S(1)) and 2.713(2) (Ag–S(2)) Å as in octahedrally coordinated Ag(I) complexes with mixed N,S donor and pure S donor macrocycles [22–26]. The equatorial Ag–N distances, 2.367(5) and 2.392(6), are 0.14 Å shorter than the axial bond Ag–N(3) of 2.522(6) Å. The Ag–N distances agree well with literature data [25, 26]. As can be taken from the N–Ag–N bond angles, the coordination of the triaza fragment is exactly intermediate between the meridional arrangement observed in the Cu(II) complex and the facial arrangement found in the Ni(II) complex.

The overall conformation — reflected in the torsional angles (see Table 6) — of the macrocycle L^1 is different in the complexes under study. Within a ten-membered fragment from C(3) to N(3) the ligand conformation in $[CuL^1](ClO_4)_2$ and $[NiL^1(H_2O)](ClO_4)_2$ is very similar, but totally different in the remaining part (see also Figs. 1 and 2), due to the different coordination of the N_3 fragment. The torsional angles deviate considerably from ideal 180 or 60° for the aliphatic segments of the ligand in these two complexes. The meridional coordination of the N_3 fragment in $[CuL^1](ClO_4)_2$ seems to impose less strain to the ligand than the facial coordination. Probably the greater thermodynamic stability of $[CuL^1]^{2+}$ in relation to $[CuL^3]^{2+}$ can be ascribed to this coordination mode.

In contrast to the Ni(II) and Cu(II) complexes the torsional angles within the ligand of $[AgL^1](ClO_4)$ are generally closer to the ideal values, because the d^{10} ion Ag(I) does not show a strong preference for any coordination polyhedron. Within a ten-membered fragment from C(1) to C(11) the torsional angles at chemically equivalent atoms differ only slightly. The free ligand seems already to be well preoriented for complex formation with Ag(I).

In $[CuL^1](ClO_4)_2$ and $[NiL^1(H_2O)](ClO_4)_2$ the conformation of the adjoining five-membered chelate rings are $\delta\lambda$ (or $\lambda\delta$), whereas it is $\lambda\lambda$ (or $\delta\delta$) in $[AgL^1](ClO_4)$. In complexes of 1,4,7-triazacyclononane the small ring size requires $\delta\delta\delta$ (or $\lambda\lambda\lambda$) conformations.

TABLE 6. Torsional angles within the ligand L^1

	$[CuL^1]^{2+}$	$[NiL^1]^{2+}$	$[AgL^1]^+$
C(8)···C(9)	−57.3	−65.1	−58.1
C(9)···S(2)	+143.3	+153.1	−61.4
S(2)···C(10)	−63.7	−77.3	+161.8
C(10)···C(11)	−3.7	+7.9	+1.3
C(11)···C(16)	−61.6	−68.3	−81.0
C(16)···N(3)	−60.1	−55.5	−177.0
N(3)···C(17)	+160.2	+105.1	−73.3
C(17)···C(18)	−48.6	+45.1	−60.6
C(18)···N(2)	+171.5	+78.0	−81.1
N(2)···C(19)	−156.9	−96.2	−162.4
C(19)···C(20)	+57.6	−47.0	−67.2
C(20)···N(1)	+179.9	+177.4	+179.8
N(1)···C(1)	−161.3	+162.2	−70.8
C(1)···C(2)	−52.8	+67.5	−78.8
C(2)···C(3)	−10.1	+1.5	+1.9
C(3)···S(1)	−71.0	−156.1	+162.8
S(1)···C(8)	+154.2	+165.5	−62.9

In the structures of $[CuL^1](ClO_4)_2$ and $[NiL^1(H_2O)](ClO_4)_2$ the perchlorate ions are disordered, as shown by some large anisotropic temperature parameters. Four hydrogen bonds (with lengths from 2.941 to 3.101 Å) between NH groups and ClO_4^- ions are observed in the structure of $[CuL^1](ClO_4)_2$, only one (3.102 Å) in the structure $[AgL^1](ClO_4)$. No hydrogen bonds are present in the structure of the Ni(II) complex, and no short intramolecular contacts have been found in any structure.

Supplementary material

Tables of complete crystallographic data, bond distances and angles, and thermal parameters are available from the authors on request.

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