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Silver, copper and nickel complexes of 1-oxa-4,7-dithiacyclononane and 1-oxa-4,8-dithiacyclodecane

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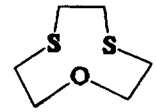
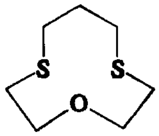
Abstract—The complexes $[Ag(L1)(PPh_3)][CF_3SO_3]$, $[Cu(L1)(PPh_3)][ClO_4]$ and $[Ni(L2)_2][ClO_4]_2$ have been prepared. L1 = 1-oxa-4,7-dithiacyclononane and L2 = 1-oxa-4,8-dithiacyclodecane. NMR, conductance and electrochemical properties are described. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: macrocycles; thioethers; metal complexes; X-ray structures.

The appearance in 1981 of Murray and Hartley's review [1] of the coordination chemistry of thioethers provoked considerable interest in them as monodentate and eventually as polydentate donors. Since that time, a substantial body of knowledge has been accumulated concerning these donors in both cyclic and acyclic ligands and this knowledge has begun to appear in current reviews [2,3]. More recently, interest in modification of complex properties by incorporation of other donors, in particular nitrogen, has become apparent [4–7] but little effort has been devoted to ethereal oxygen as a modifier [8,9]. As part of our long term interest in complexes of thioether [10] and modified thioether ligands [11], we have examined the structures and a few properties of nickel, copper and silver complexes of L1 and L2 that contain both ether and thioether donors as well as phosphine donors in some cases. The results are compared to those from studies of other related N,S-donor macrocyclic ligand complexes.



L1



L2

EXPERIMENTAL

Commercially available reagents were obtained from the Aldrich Chemical Co. Inc., or from Morton Thiokol Alfa Products Inc. and were used without further purification. Preparations for ligands L1 and L2 have been reported previously [10,12]. NMR data were obtained by using a General Electric 300-NB instrument. Magnetic susceptibility data were obtained at room temperature by the Faraday method. The calibrant was $HgCo(NCS)_4$. Electrochemical measurements were carried out under a nitrogen atmosphere at room temperature by using a Cypress Systems, Inc., CS-1087 computer-controlled potentiostat. Solution concentrations were 10^{-3} mol/L in complex and 0.1 mol/L in supporting electrolyte (tetraethylammonium perchlorate). Voltammograms were recorded in acetonitrile by using a glassy carbon working electrode that was pre-polished with 0.3 μm Al_2O_3, a platinum counter electrode and an aqueous saturated calomel reference electrode checked periodically relative to a 1.0×10^{-3} mol/L solution of ferrocene in acetonitrile containing 0.1 mol/L tetraethylammonium perchlorate for which the ferrocene/ferrocenium reduction potential was 400 mV. The ref-

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erence electrode was separated from the bulk of the solution by a porous Vycor tube. Junction potential corrections were not used. Conductance data were obtained by using a General Radio Co. Type 1605-AH bridge with impedance comparator and a constant-temperature bath adjusted to 25°C. X-ray diffraction data were collected by using a Rigaku AFC6S diffractometer. Analyses were performed by Canadian Microanalytical Service Ltd.

Preparation

$[Ag(L1)(PPh_3)][CF_3SO_3]$. Solutions of L1 (66 mg, 0.40 mmol) in methanol (5 cm^3) and $AgCF_3SO_3$ (103 mg, 0.400 mmol) in methanol (5 cm^3) were mixed and stirred for 5 min. To this solution was added $P(C_6H_5)_3$ (105 mg, 0.400 mmol) in methanol (10 cm^3). The resulting solution was allowed to evaporate slowly to a final volume of ~ 2 cm^3 when colourless crystals formed that were collected and washed with a little cold methanol and dried in air. Yield: 129 mg (47%). Anal. calcd for $C_{25}H_{27}AgF_3O_4PS_3$: C, 43.93; H, 3.98. Found: C, 43.54; H, 3.80. NMR ($CDCl_3$, in ppm from TMS int. std.), ^1H; 7.47 (m, 15H) C_6H_5, 3.68 (t, $J = 5.1$ Hz, 4H) $—CH_2OCH_2—$, 3.09 (s, 4H) $—SCH_2CH_2S—$, 2.84 (t, $J = 5.1$ Hz, 4H) $—CH_2SCH_2CH_2SCH_2—$.

$[Cu(L1)(PPh_3)][ClO_4]$. Solutions of L1 (82 mg, 0.50 mmol) in acetonitrile (10 cm^3) and $[Cu(CH_3CN)_4][ClO_4]$ (164 mg, 0.500 mmol) in acetonitrile (10 cm^3) were mixed and refluxed with stirring for 2 h before being cooled to room temperature. To the solution was added $P(C_6H_5)_3$ (131 mg, 0.500 mmol) in acetonitrile (5 cm^3). The solution was allowed to evaporate slowly to a final volume of ~ 4 cm^3 when colourless crystals formed that were separated, washed with a small amount of acetronitrile and dried in air. Yield: 215 mg (73%). Anal. calcd for $C_{24}H_{27}ClCuO_5PS_2$: C, 48.89; H, 4.62. Found: C, 48.70; H, 4.65.

$[Ni(L2)_2][ClO_4]_2$. A solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (180 mg, 0.492 mmol) in methanol (5 cm^3) to which was added nitromethane (20 cm^3) was mixed with a solution of L2 (178 mg, 1.00 mmol) in nitromethane (10 cm^3). The deep blue solution that formed was filtered and left standing to evaporate solvent slowly until blue needle-like crystals formed. These were collected, washed with small amounts of dichloromethane, acetone and finally diethyl ether and dried in air. Yield: 212 mg (69%). Anal. calcd for $C_{14}H_{28}Cl_2NiO_{10}S_4$: C, 27.38; H, 4.59; S, 20.88; Ni, 9.56. Found: C, 27.29; H, 4.59; S, 20.39; Ni, 9.06. $\mu_{eff} = 2.98$ B.M. (22°C). ($\Lambda_M = 230$ ohm^{-1} cm^2 mol^{-1} in nitromethane at 4.6×10^{-4} mol/L).

X-ray studies

A summary of crystallographic data for $[Ag(L1)(PPh_3)][CF_3SO_3]$, $[Cu(L1)(PPh_3)][ClO_4]$ and $[Ni(L2)_2][ClO_4]_2$ is in Table 1. The diffraction intensities were collected at 299 K by the ω–2θ scan technique at a scan speed of 8°/min to a maximum 2θ value of 50.1°. Three standards were measured after every 150 reflections and no significant crystal decay was detected. The space groups were determined by systematic absences, packing considerations, a statistical analysis of intensity distribution and the successful solution and refinement of the structures. Unit cell parameters (Table 1) were determined by a least squares refinement of the setting angles for 19 reflections in the range $41.68 \leqslant 2\theta \leqslant 44.82°$ ($[Ag(L1)(PPh_3)][CF_3SO_3]$), 20 reflections in the range $38.43 \leqslant 2\theta \leqslant 43.35°$ ($[Cu(L1)(PPh_3)][ClO_4]$) and 18 reflections in the range $25.86 \leqslant 2\theta \leqslant 38.34°$ ($[Ni(L2)_2][ClO_4]_2$). Lorentz and polarization factors were applied and corrections were made for absorption. The structures were solved by direct methods [13,14] and refined by full matrix least-squares [15] with counting statistics weights. H-atom positions were calculated then refined and the hydrogens were assigned isotropic thermal parameters 20% greater than those of their bonding partners but the thermal parameters were not refined. H-atom positions were fixed for the final round of least squares refinement. Non-hydrogen atoms were refined anisotropically except in the structure of $[Cu(L1)(PPh_3)][ClO_4]$ where the ClO_4^- ion was refined isotropically and in the structure of $[Ni(L2)_2][ClO_4]_2$ where the disordered carbon, C(6), and most of the perchlorate oxygens were refined isotropically. The final cycle of refinement was based on 4032 observed reflections $[I > 2.00\sigma(I)]$ and 380 variables ($[Ag(L1)(PPh_3)][CF_3SO_3]$), 1232 observed reflections $[I > 2.00\sigma(I)]$ and 105 variables ($[Cu(L1)(PPh_3)][ClO_4]$) and 1348 observed reflections $[I > 2.00\sigma(I)]$ and 139 variables ($[Ni(L2)_2][ClO_4]_2$) and converged. All calculations were performed with the TEXSAN crystallographic software package [16] of Molecular Structure Corporation. Scattering factors were taken from the usual source [17].

RESULTS AND DISCUSSION

The structure of $[Ag(L1)(PPh_3)][CF_3SO_3]$ is shown in Fig. 1 while selected bond lengths and angles are in Table 2.

There is a distorted pseudo-tetrahedral array of donor atoms about the silver with bond angles that lie in the range 85.41(4)–140.31(3)°. Angles at silver also involving atoms within the heterocyclic ring are all less than 86° due to formation of chelate rings whereas those between ring donors and the phosphorus atom are all greater than 113° and one [P—Ag—S1 = 140.31(3)°] is much greater. The range and magnitude of these angles are not unlike those reported for $[Ag_2L_2]^{2+}$ (L = 2,5,8,11-tetrathia[12](2,5)thiophenophane) [18]. The Ag—S bond lengths in $[Ag(L1)(PPh_3)][CF_3SO_3]$ [2.552(1), 2.572(1) Å] can be compared with those in $[Ag_2L_2]^{2+}$ (L = 2,5,8,11-

Table 1. Crystallographic data for $[Ag(L1)(PPh_3)][CF_3SO_3]$, $[Cu(L1)(PPh_3)][ClO_4]$ and $[Ni(L2)_2][ClO_4]_2$

	$[Ag(L1)(PPh_3)][CF_3SO_3]$	$[Cu(L1)(PPh_3)][ClO_4]$	$[Ni(L2)_2][ClO_4]_2$
Chem formula	$C_{25}H_{27}AgF_3O_4PS_3$	$C_{24}H_{27}ClCuO_5PS_2$	$C_{14}H_{28}Cl_2NiO_{10}S_4$
Fw		589.28	614.22
Space group	$P\bar{1}$ (#2)	$R\bar{3}$(h) (#148)	$R\bar{3}c$(h) (#167)
a (Å)	10.888(2)	11.044(4)	18.204(3)
b (Å)	14.529(3)		
c (Å)	10.247(4)	36.869(2)	38.023(9)
α (°)	108.47(2)		
β (°)	93.89(3)		
γ (°)	109.83(2)		
ρ_{calcd} (g cm^{-3})		1.507	1.682
V (Å^3)		3894(3)	10913(4)
Z		6	18
λ (Å)	0.71069	0.71069	0.71069
μ (cm^{-1})		12.28	14.01
R^a (%)		0.048	0.062
$R_w{}^b$ (%)		0.055	0.056

^{a} $R = \Sigma \| F_o| - |F_c \| / \Sigma |F_o|$.

^{b} $R_w = [(\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2)]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°) in $[Ag(L1)(PPh_3)][CF_3SO_3]$

Ag—S(1)	2.552(1)	Ag—S(2)	2.572(1)
Ag—P(1)	2.3697(9)	Ag—O(1)	2.640(3)
S(1)—Ag—S(2)	85.41(4)	S(1)—Ag—P(1)	140.31(3)
S(2)—Ag—P(1)	134.24(3)	P(1)—Ag—O(1)	113.85(6)
S(1)—Ag—O(1)	72.94(7)	S(2)—Ag—O(1)	74.31(6)

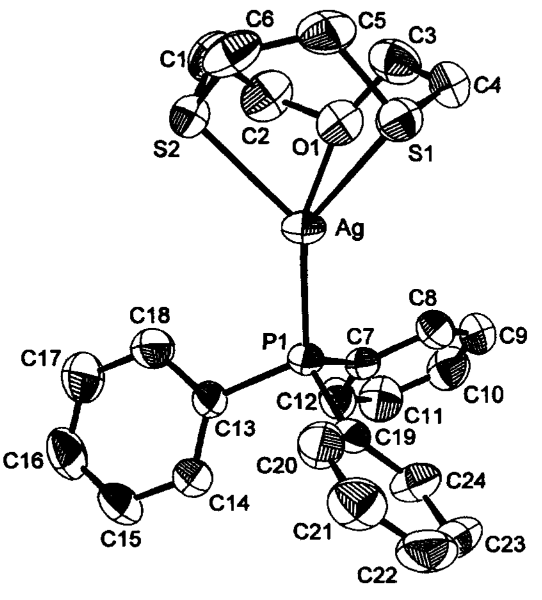

Fig. 1. The structure of $[Ag(L1)(PPh_3)]^+$.

tetrathia[12](2,5)thiophenophane) [18] which have an average length of 2.695 Å and a range of 2.564–2.995 Å. The Ag—P length [2.3697(9) Å] can be compared with that in *anti*-$[Ag_2(L')(PPh_3)_2]^{+2}$ (L′ = 2,5,8,17,20,23-hexathia[9](1,2)[9](4,5)cyclophane) [19] which is 2.407(3) Å and the Ag—O distance [2.640(3) Å] with that in $[(CH_2O)_6Ag_2][Ag][AsF_6]_3$ [2.458(5) Å] [20] or those in $[Ag([15]aneS_2O_3)]^+$ [2.667(5), 2.690(4), 2.492(4) Å] [21]. The conformation adopted by the ligand is [3,3,3] as a result of the interaction of the ether oxygen with the silver atom.

The structure of $[Cu(L1)(PPh_3)][ClO_4]$ is shown in Fig. 2 and selected bond lengths and angles are in Table 3.

The heterocyclic ligand is disordered about a three-fold axis with a chalcogen and two carbon atoms in the asymmetric unit. It was not possible to model the fragments separately so ‘S(1)’ represents 2/3 of a sulfur atom and 1/3 of an oxygen atom modelled with a 5/6 sulfur occupancy. Similarly C(7) and C(8) are a 2/3–1/3 superposition of two different methylene carbons which is reflected in the high thermal parameters of the two ‘atoms’. The coordination geometry around copper is pseudo-tetrahedral with

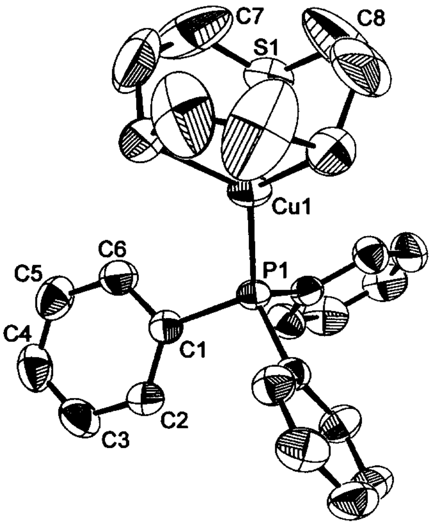

Fig. 2. The structure of $[Cu(L1)(PPh_3)]^+$.

bond angles at copper of 89.01(6)° for those within chelate rings while those involving the phosphorus atom are 125.96°. The bond lengths for all three Cu–L1 bonds have been determined to be the same [2.334(2) Å] while the Cu—P distance is found to be 2.188(2) Å. These may be compared to the Cu—S distances in $[Cu(3,6\text{-dithiaoctane})_2]^+$ which vary from 2.280(4) to 2.318(5) with an average of 2.303 Å [22] and to those in $[Cu(L)_2]^+$ (L = 2,5,8-trithia[9](2,5)thiophenophane) [23] which range from 2.301(3) to 2.392(3) with an average of 2.340 Å. Likewise, the Cu—P distance can be compared to those of 2.262(9) and 2.272(6) Å in $[(Cy_3P)_2(pzH)Cu]ClO_4 \cdot CH_3OH$ [24] or 2.190(2), 2.252(3) and 2.260(3) Å in $[Cu_2Br_2(PPh_3)_3]$ [25]. In the latter, one Ph_3P is in a sterically unencumbered position much like that in $[Cu(L1)(PPh_3)][ClO_4]$ and the corresponding Cu—P distances [2.190(2) and 2.188(2) Å] are very similar. Apparently, the change from two bridging bromines (as in $[Cu_2Br_2(PPh_3)_3]$) to two thioether and one ether (as in $[Cu(L1)(PPh_3)][ClO_4]$) as additional ligands has almost no influence on the Cu—P distance. There are few examples of Cu^I—O bond lengths in the literature but the Cu—O distance of 2.334(2) Å in $[Cu(L1)(PPh_3)][ClO_4]$ is longer than observed distances to carboxylate oxygens [1.923(5), 2.134(5), 1.945(6) and 2.107(6) Å] [26] and shorter than those to ether oxygens [27] [2.510(11) and 2.432(8) Å]. The Cu—O distance in $[Cu(L1)(PPh_3)][ClO_4]$ is also longer than those of 1.917(9) and 2.015(11) Å in the mixed-valence compound $[Cu_3Br_4(DMF)_2(H_2O)]_n$ in which the formal oxidation state of the copper atoms is on average 1.33 [28]. In fact, this distance is not unlike that in the Cu^{II} complex $CuCl_2 \cdot L$ (L = 1,9-bis(2-thienyl)-5-oxa-2,8-dithianonane) [11] [2.30(1) Å] which illustrates the ability of Cu to accommodate changes in oxidation state with or without a change in bond length in a manner reminiscent of its accommodating behaviour noted above with respect to bonds to phosphorus. The conformation of the ligand in this structure is [3,3,3], similar to that found in the analogous silver complex (*vide supra*) as a result of interaction between the oxygen atom of the ligand and the copper atom.

The structure of $[Ni(L2)_2][ClO_4]_2$ is shown in Fig. 3 and selected bond lengths and angles are in Table 4. The Ni—S lengths in pseudo-octahedral $[Ni(L2)_2][ClO_4]_2$ are 2.353(2) and 2.390(2) Å. The Ni—O bonds, which are not mutually *trans*, are 2.115(5) Å long. The larger Ni—S distance is typical of those in

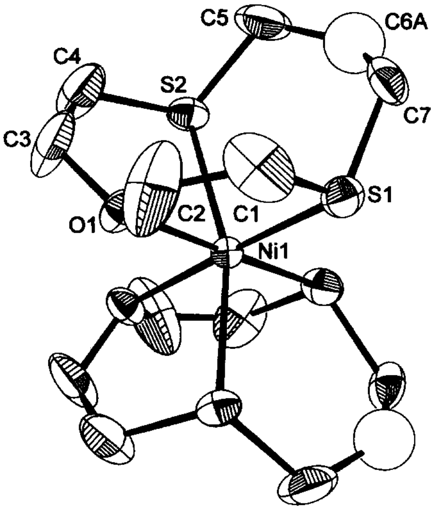

Fig. 3. The structure of $[Ni(L2)_2]^{2+}$.

Table 3. Selected bond lengths (Å) and angles (°) in $[Cu(L1)(PPh_3)][ClO_4]$

S(1)—Cu—S(2)	89.01(6)	S(1)—Cu—S(2)	89.01(6)
S(1)—Cu—O	89.01(6)	S(1)—Cu—P(1)	125.96(4)
S(2)—Cu—O	89.01(6)	S(2)—Cu—P(1)	125.96(4)
O—Cu—P(1)	125.96(4)		
Cu—S(1)	2.334(2)	Cu—S(2)	2.334(2)
Cu—O	2.334(2)	Cu—P(1)	2.188(2)

Table 4. Selected bond lengths (Å) and angles (°) in $[Ni(L2)_2][ClO_4]_2$

Ni—S(1)	2.353(2)	Ni—S(2)	2.390(2)
Ni—O(1)	2.115(5)		
S(1)—Ni—S(1)*	100.8(1)	O(1)—Ni—S(1)*	173.2(2)
S(2)—Ni—O(1)*	84.98(8)	O(1)—Ni—O(1)*	91.0(3)
S(2)—Ni—S(1)*	91.41(6)	S(2)—Ni—S(2)*	163.2(1)
S(1)—Ni—S(2)	99.34(8)	S(2)—Ni—O(1)*	85.0(2)
S(1)—Ni—O(1)	84.3(2)	S(2)—Ni—O(1)	83.2(2)

both linear [29] and cyclic [10] polythioether complexes. The smaller, however, is significantly shorter than the average length (2.43 Å) [1] of Ni—S bonds found in octahedral monodentate ligand complexes and slightly shorter than the usual range of lengths in cyclic ligand complexes as, for example, in $[Ni(9S3)_2]^{2+}$ [2.375(3)–2.400(5) Å] (9S3 = 1,4,7-trithiacyclononane) [30]. The general shortening is probably due to compression caused by use of a cyclic ligand while the extreme shortening may arise from the fact that the bond involved [Ni—S(1)] is *trans* to an ether oxygen. If thioethers participate in π-acid bonding whereas ethers do not, this would be the result expected. The Ni—O distance is unremarkable [29,31]. Bond angles range from 83.2(2) to 99.34(8)° and the greatest deviation from linearity across the Ni atom involves the angle S(2)—Ni—S(2) which is 163.2(1)°.

Coordination of L1 to Ag in $[Ag(L1)(PPh_3)]$ $[CF_3SO_3]$ produces a negligible (0.02, 0.04 ppm) shift in the nmr resonance frequencies (compared to the free ligand) [12] of hydrogens adjacent to the metal-bound thioether sites but a much larger (0.27 ppm) shift for hydrogens adjacent to the ethereal oxygen. This confirms the indication in the X-ray study that the oxygen atom is interacting with the silver atom. Coordination of the ligand also changes the coupling constants in the apparent triplet signals from 9.6 Hz in the free ligand to 5.1 Hz in the complex.

The cyclic voltammetric response of $[Ni(L2)_2]$ $[ClO_4]_2$ is very similar to that of its analogue with $[20]aneO_2S_4$ [10], the dimer of L2. That ligand supplies the same O_2S_4 donor set as two equivalents of L2 but in a single ring. Thus, $[Ni(L2)_2][ClO_4]_2$ is electrochemically silent between -0.7 and $+0.7$ V *vs* SCE unless the initial potential is set at less than -0.7 V or a scan into that region precedes a scan to $> +0.7$ V. Under the latter conditions, a wave at $+0.23$ V *vs* SCE occurs followed by a reduction wave at -1.06 V and then a minor return wave at -0.75 V and finally the major wave at $+0.23$ V *vs* SCE. On the basis of these observations, metal-based oxidation seems relatively unfavourable and the observed reduction is irreversible.

The conductivity of $[Ni(L2)_2][ClO_4]_2$ is roughly that of the 1:2 electrolytes, $[Ni(L)(H_2O)][ClO_4]_2 \cdot CH_3OH$, ($\Lambda_M = 205$ ohm^{-1} cm^2 mol^{-1} in acetonitrile at 5.0×10^{-4} mol/L) (L = 1,9-bis(2-pyridyl)-2,5,8-trithianonane) [29] and $[Co(L')][ClO_4]_2$ ($\Lambda_M = 199$ ohm^{-1} cm^2 mol^{-1}) (nitromethane; 2.5×10^{-4} mol/L) (L′ = 1,12-bis(2-pyridyl)-2,5,8,11-tetrathiadodecane) [32] the structures and properties of which we have reported previously.

CONCLUSIONS

The ligand 1-oxa-4,7-dithiacyclononane (L1) adopts a [3,3,3] conformation in both the Ag^I and Cu^I complexes examined in this study and in this respect it resembles other $[9]aneX_3$ (X = N,S) ligands [33,34]. The interaction of ethereal oxygen with Cu^I and Ag^I by L1 is also observed in the behaviour of L2 with nickel. Thus, addition of an extra methylene to the ring does not alter substantially the ligands' coordination behaviour. In the literature, there are few X-ray structures of Cu^I or Ag^I involving ether or phosphine ligands and fewer still that have thioether donors as well, and it is usually argued that Cu^I and Ag^I being 'soft' acids should have little affinity for the 'hard' base oxygen. The present results are therefore significant in the sense that they show both thioether and ether donors coordinated to Cu^I and Ag^I. The X-ray structure of $[Ni(L2)_2][ClO_4]_2$ provides further evidence of the π-bonding capability of thioether sulfur through the observation of its short Ni—S bond *trans* to —O— compared to the longer Ni—S distance *trans* to —S—.

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