

Metal Complexes of 1-Oxa-4,7-dithiacyclononane

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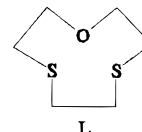
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The ligand 1-oxa-4,7-dithiacyclononane (L) and its complexes [Pd(L)Cl₂], [Cu(L)₂][ClO₄]·CH₃CN, [Cu(L)Br]₂, and [Co(L)₂][ClO₄]₂·2CH₃NO₂ have been prepared. Crystal data are as follows. For monoclinic [Pd(L)Cl₂], C₆H₁₂Cl₂OPdS₂: space group *P2*₁/*n*; *a* = 8.464(2), *b* = 12.199(2), *c* = 10.384(2) Å; β = 105.09(1)°; *Z* = 4; *R* = 0.024, *R*_w = 0.033 for 1721 reflections. For monoclinic [Cu(L)₂][ClO₄]·CH₃CN, C₁₄H₂₇ClCuNO₆S₄: space group *P2*₁/*n*; *a* = 7.743(2), *b* = 19.515(5), *c* = 15.017(2) Å; β = 102.85(2)°; *Z* = 4; *R* = 0.036, *R*_w = 0.038 for 3124 reflections. For triclinic [Cu(L)Br]₂, (C₆H₁₂BrCuOS₂)₂: space group *P* $\bar{1}$; *a* = 7.809(5), *b* = 8.880(3), *c* = 7.567(2) Å; α = 92.44(3), β = 102.85(2), γ = 99.30(4)°; *Z* = 2; *R* = 0.027, *R*_w = 0.027 for 1494 reflections. For monoclinic [Co(L)₂][ClO₄]₂·2CH₃NO₂, C₁₄H₃₀Cl₂CoN₂O₁₄S₄: space group *P2*₁/*c*; *a* = 10.333(3), *b* = 14.293(6), *c* = 9.365(4) Å; β = 100.89(3)°; *Z* = 2; *R* = 0.067, *R*_w = 0.058 for 1517 reflections. The ligand displays a variety of conformations in these structures. The palladium complex does not undergo 1,4-heteroatom binding site fluxional processes but does dissociate in dimethyl sulfoxide. An apical Pd···O (2.968(3) Å) interaction has been detected by both NMR and X-ray studies. The Cu(I) cation is tetrahedral with a [2+2] mode of ligand coordination. [Cu(L)Br]₂ involves two Br bridges between coppers and two thioether sulfurs from a ligand to complete each copper's tetrahedral coordination sphere. Surprisingly, the cyclic voltammetric behavior of the copper complexes is similar to that of 1,4,7-trithiacyclononane complexes. The cation [Co(L)₂]²⁺ is pseudo-octahedral with nearly regular angles at cobalt but a long (2.235(6) Å) Co–O bond due to Jahn–Teller distortion. The complex [Co(L)₂][ClO₄]₂ is magnetically dilute and low-spin over the temperature range 5–292 K.

Introduction

Thiocrown ethers as ligands have been studied intensively for over a decade, and from time to time during that period, reviews of progress in the field have appeared.^{1–3} More recently, interest in differences in the properties of metal complexes caused by replacement of one or more thioether sulfurs with amine nitrogen atoms has been apparent in the literature.^{4–9} In spite of this and the obvious connection between crown ethers and thiocrown ethers, less effort, until quite recently,^{10–14} has been devoted to a comparison of O,S donor complexes with complexes of these other ligand systems. As part of our continuing interest in the properties of both acyclic and cyclic ligands that have thioether and other

donors,^{15–18} we have examined the properties of some metal complexes of ligand L and the results are reported herein for the purpose of comparison with those from homothioether and mixed S,N donor macrocyclic ligand complexes.



Experimental Section

Commercially available reagents were obtained from the Aldrich Chemical Co. Inc. or from Morton Thiokol Alfa Products Inc. and were used without further purification. Those used for cyclic voltammetry measurements were of spectroscopic grade. Spectroscopic data were obtained by using the following instruments: IR, Mattson Polarix FT; UV/vis, Cary Model 17; NMR, General Electric 300-NB. Magnetic susceptibility data were obtained at room temperature by the Faraday method. Variable-temperature magnetic susceptibility data on powder samples were obtained in the range 5–292 K by using an Oxford Instruments superconducting Faraday magnetic susceptibility system with a Sartorius 4432 microbalance. Main solenoid fields of 1.5 and 2.0 T and a gradient field of 10 T m⁻¹ were employed, and the susceptibility data were corrected for diamagnetism by using Pascal's constants. 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

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Table 1. Crystallographic Data for [Pd(L)Cl₂], [Cu(L)₂][ClO₄] \cdot CH₃CN, [Cu(L)Br]₂, and [Co(L)₂][ClO₄]₂ \cdot 2CH₃NO₂

	[Pd(L)Cl ₂]	[Cu(L) ₂][ClO ₄] \cdot CH ₃ CN	[Cu(L)Br] ₂	[Co(L) ₂][ClO ₄] ₂ \cdot 2CH ₃ NO ₂
empirical formula	C ₆ H ₁₂ Cl ₂ OPdS ₂	C ₁₄ H ₂₇ ClCuO ₆ S ₄ N	C ₆ H ₁₂ BrCuOS ₂	C ₁₄ H ₃₀ Cl ₂ CoN ₂ O ₁₄ S ₄
fw	341.59	532.61	307.73	708.48
space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 1 (No. 2)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>T</i> , °C	26	26	26	-88
<i>a</i> , Å	8.464(2)	7.743(2)	7.809(5)	10.333(3)
<i>b</i> , Å	12.199(2)	19.515(5)	8.880(3)	14.293(6)
<i>c</i> , Å	10.384(2)	15.017(2)	7.567(2)	9.365(4)
α , deg			92.44(3)	
β , deg	105.09(1)	102.85(2)	100.32(3)	100.89(3)
γ , deg			99.30(4)	
ρ_{calcd} , g cm ⁻³	2.192	1.599	2.011	1.732
<i>V</i> , Å ³	1035.2(3)	2212.4(9)	508.1(4)	1358(2)
<i>Z</i>	4	4	2	2
λ , Å	0.710 69	0.710 69	0.710 69	0.710 69
μ , cm ⁻¹	26.32	15.02	63.93	11.88
<i>R</i> _s ^a %	0.024	0.036	0.027	0.067
<i>R</i> _w ^b %	0.033	0.038	0.027	0.058

$$^a R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b R_w = \frac{[\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}}$$

working electrode that was prepolished with 0.3 μ m Al₂O₃, a platinum counter electrode, and an aqueous saturated calomel reference electrode checked periodically relative to a 1.0 \times 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 reference electrode was separated from the bulk of the solution by a porous Vycor tube. Junction potential corrections were not used. Analyses were performed by Canadian Microanalytical Service Ltd.

Preparative Details. *Caution!* Although we have experienced no problems while handling any of the substances described herein, readers are cautioned to exercise appropriate care when handling perchlorates, which are treacherously prone to explode violently.

C₆H₁₂OS₂, Ligand L. This preparation was carried out under an inert atmosphere of dry nitrogen. Cesium carbonate (14.5 g, 45 mmol) was dried in an oven at 80 °C for 10 h, finely powdered, and transferred to a 2 L three-necked flask equipped with a mechanical stirrer. *N,N*-Dimethylformamide (DMF) (300 mL, from a freshly opened bottle) was deaerated and transferred to the 2L reaction flask. The reaction mixture was stirred vigorously and its temperature adjusted to 80 °C. A solution of bis(2-mercaptoethyl) ether (4.9 g, 36 mmol) and 1,2-dibromoethane (6.7 g, 36 mmol) in deaerated DMF (300 mL) was added from a dropping funnel at the rate of 6–8 mL/h under a nitrogen atmosphere. After the addition was complete, stirring was continued at 80 °C for a further 12 h. DMF was removed, and the yellow residue was suspended in water (100 mL) and extracted with dichloromethane (3 \times 100 mL). The combined extracts were washed with 1.0 mol L⁻¹ aqueous NaOH (100 mL) and then water (2 \times 100 mL) and dried over anhydrous sodium sulfate. After removal of the solvent, ethanol (200 mL) was added to the brown viscous mixture, and the resultant mixture was filtered. The filtrate was concentrated to a brown oil by using a rotary evaporator. The product, ligand L, was purified by vacuum distillation and the fraction with bp 85–90 °C/0.5 mm was collected. Yield: 2.3 g (39%). NMR (ppm from TMS internal standard, CDCl₃): ¹H 3.95 (t, *J* = 9.6 Hz, 4H, -CH₂O), 3.07 (s, 4H, -SCH₂-CH₂S-), 2.80 (t, *J* = 9.6 Hz, 4H, -CH₂S); ¹³C (proton decoupled) 73.7 (CH₂O), 34.6 (SCH₂-), 33.2 ((CH₂S)₂). MS: calcd for C₆H₁₂-OS₂, *m/z* = 164.0329; found, *m/z* 164.0330.

[Pd(L)Cl₂]. A solution of ligand L (112 mg, 0.683 mmol) in acetonitrile (10 mL) was added to a solution of *cis*-PdCl₂(PhCN)₂ (230 mg, 0.600 mmol) in acetonitrile (20 mL). The orange precipitate that formed immediately was filtered off, washed with acetonitrile and diethyl ether, and dried in vacuum. Yield: 180 mg (88%). Anal. Calcd for C₆H₁₂Cl₂OPdS₂: C, 21.10; H, 3.54. Found: C, 21.20; H, 3.60.

[Cu(L)₂][ClO₄] \cdot CH₃CN. A solution of [Cu(CH₃CN)₄]ClO₄ (65 mg, 0.20 mmol) in acetonitrile (10 mL) was added to a solution of ligand L (65 mg, 0.40 mmol) in acetonitrile (5 mL) under a dry nitrogen atmosphere. The mixture was stirred at 50 °C for 2 h. The resulting yellow-green solution was filtered, and the filtrate was left to evaporate slowly. The colorless crystals that formed were collected by filtration, washed with dichloromethane, and dried under vacuum. Yield: 83.5 mg (78.4%). NMR (ppm from TMS internal standard, CD₃CN): ¹H

3.85 (t, *J* = 5.0 Hz, 4H, CH₂O), 3.07 (s, 4H, SCH₂CH₂S), 2.81 (t, *J* = 5.0 Hz, 4H, CH₂S), 1.93 (m, CH₃CN). Anal. Calcd for C₁₄H₂₇-ClCuNO₆S₄: C, 31.57; H, 5.12; N, 2.62. Found: C, 31.69; H, 5.12; N, 2.57.

[Cu(L)Br]₂. A solution of CuBr (72 mg, 0.50 mmol) in acetonitrile (15 mL) was added to a solution of ligand L (98 mg, 0.57 mmol) in acetonitrile (20 mL). A yellow precipitate appeared but redissolved after the mixture was refluxed for 2 h with stirring. The solution was allowed to cool to room temperature, resulting in precipitation of a gray crystalline solid. The precipitate was isolated, washed with ethanol, and recrystallized from acetonitrile to give 108 mg (70%) of [Cu(L)Br]₂ as colorless crystals. Anal. Calcd for C₆H₁₂BrCuOS₂: C, 23.42; H, 3.93. Found: C, 23.58; H, 3.93.

[Co(L)₂][ClO₄]₂. Solutions of ligand L (98.5 mg, 0.600 mmol) in methanol (10 mL) and Co(ClO₄)₂ \cdot 6H₂O (110 mg, 0.301 mmol) in methanol (10 mL) were mixed and refluxed for 12 h. The resulting solution was cooled and filtered, and the filtrate was allowed to evaporate slowly until red needles formed. These were separated from the mixture washed with methanol and then diethyl ether, and dried in air. Yield: 157 mg (89%). Anal. Calcd for C₁₂H₂₄Cl₂CoO₁₀S₄: C, 24.58; H, 4.12. Found: C, 24.96; H, 4.19. Crystals suitable for X-ray studies were obtained by recrystallization from CH₃NO₂ by diethyl ether vapor diffusion.

X-ray Studies. A summary of crystallographic data for [Pd(L)-Cl₂], [Cu(L)₂][ClO₄] \cdot CH₃CN, [Cu(L)Br]₂, and [Co(L)₂][ClO₄]₂ \cdot 2CH₃-NO₂ is given in Table 1. The diffraction intensities were collected at 299 K except for those from [Co(L)₂][ClO₄]₂ \cdot 2CH₃NO₂, which were collected at 185 K. Collection was performed by the ω -2 θ scan technique at a scan speed of 8°/min to a maximum 2 θ value of 50.1°. Three standards were measured after every 150 reflections, and no significant crystal decay was detected. The space group was determined by systematic absences, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure. Unit cell parameters (Table 1) were determined by a least-squares refinement of the setting angles for 17 reflections in the range 49.32° \leq 2 θ \leq 49.79° ([Pd(L)Cl₂]), 19 reflections in the range 42.64° \leq 2 θ \leq 47.42° ([Cu(L)₂][ClO₄] \cdot CH₃CN), 17 reflections in the range 20.10° \leq 2 θ \leq 24.65° ([Cu(L)Br]₂), and 18 reflections in the range 38.20° \leq 2 θ \leq 44.17° ([Co(L)₂][ClO₄]₂ \cdot 2CH₃NO₂). Lorentz and polarization factors were applied, and corrections were made for absorption. The structures were solved by direct methods^{19,20} and refined by full-matrix least-squares routines²¹ with counting statistics weights. H atom positions were calculated then refined for the palladium complex and fixed for

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(21) Function minimized: $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o)$; $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/Lp^2$ and $S = \text{scan rate}$; $C = \text{total integrated peak count}$; $R = \text{ratio of scan time to background counting time}$; $B = \text{total background count}$; $Lp = \text{Lorentz-polarization factor}$; $p = 0.01$.

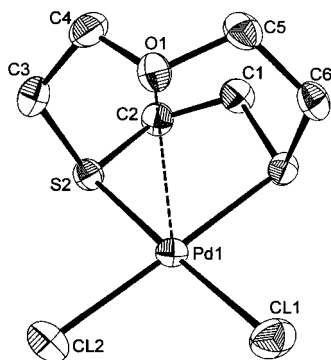


Figure 1. ORTEP of [Pd(L)Cl₂]. Thermal ellipsoids are shown at the 50% probability level.

Table 2. Selected Bond Distances and Angles in [Pd(L)Cl₂]

Distances (Å)			
Pd—Cl(1)	2.331(1)	Pd—O(1)	2.968(3)
Pd—Cl(2)	2.333(1)	Pd—S(1)	2.268(1)
Pd—S(2)	2.258(1)		
Angles (deg)			
Cl(1)—Pd—Cl(2)	93.12(4)	Cl(1)—Pd—S(1)	88.14(4)
Cl(1)—Pd—S(2)	177.93(4)	Cl(2)—Pd—S(1)	178.74(4)
Cl(2)—Pd—S(2)	88.52(4)	S(1)—Pd—S(2)	90.23(4)

the final round of least-squares refinement after earlier coordinate refinement for the other three complexes. The hydrogens were assigned isotropic thermal parameters 20% greater than those of their bonding partners, but the thermal parameters were not refined. Non-hydrogen atoms were refined anisotropically except in the structure of [Co(L)₂][ClO₄]₂·2CH₃NO₂, where the ClO₄⁻ (with the exception of its Cl atom) and CH₃NO₂ fragments were refined isotropically. The final cycle of refinement was based on 1721 observed reflections ($I > 2.00\sigma(I)$) and 146 variables ([Pd(L)Cl₂]), 3124 observed reflections ($I > 2.00\sigma(I)$) and 245 variables ([Cu(L)₂][ClO₄]₂·CH₃CN), 1494 observed reflections ($I > 2.00\sigma(I)$) and 101 variables ([Cu(L)Br]₂), and 1517 observed reflections ($I > 2.00\sigma(I)$) and 135 variables [Co(L)₂][ClO₄]₂·2CH₃NO₂ and converged. All calculations were performed with the TEXSAN crystallographic software package²² of the Molecular Structure Corp. Scattering factors were taken from the usual source.²³

Results and Discussion

The preparation of ligand L in 6% yield was reported previously from the reaction of bis(2-chloroethyl) ether with 1,2-ethanedithiol in ethanol in the presence of NaOH.²⁴ The procedure described herein using the cesium template effect gives a superior yield (39%) but depends critically on the rate and temperature of addition. Faster additions and lower temperatures reduce the yield.

Figure 1 shows the structure of [Pd(L)Cl₂], while selected bond lengths and angles are given in Table 2. Ligand L assumes a facial coordination mode in [Pd(L)Cl₂]. The Pd(II) atom lies 0.011 Å above the mean plane defined by two chloride ligands (Pd—Cl(1) = 2.331(1), Pd—Cl(2) = 2.333(1) Å) and two sulfur atoms (Pd—S(1) = 2.268(1), Pd—S(2) = 2.258(1) Å). These bond lengths compare well with those Pd—S (2.245–2.282 Å) and Pd—Cl (2.3316–2.3326 Å) found in other Pd(II) complexes of macrocyclic thioethers.^{25–27}

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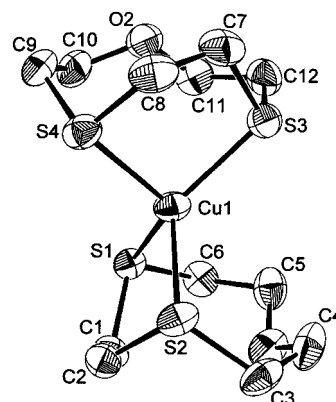


Figure 2. ORTEP of [Cu(L)₂]⁺. Thermal ellipsoids are shown at the 50% probability level.

Table 3. Ligand Torsion Angles (deg) in [Pd(L)Cl₂]

S(1)—C(1)—C(2)—S(2)	31.8(5)
S(2)—C(3)—C(4)—O(1)	-52.6(5)
C(1)—C(2)—S(2)—C(3)	81.7(4)
C(2)—C(1)—S(1)—C(6)	-126.3(3)
C(4)—O(1)—C(5)—C(6)	-130.0(4)
S(1)—C(6)—C(5)—O(1)	45.6(5)
C(1)—S(1)—C(6)—C(5)	43.9(4)
C(2)—S(2)—C(3)—C(4)	-51.0(4)
C(3)—C(4)—O(1)—C(5)	143.1(4)

The oxygen atom of L is oriented toward palladium and lies above the S₂PdCl₂ coordination plane at a Pd···O distance of 2.968(3) Å. This is rather long but is less than the sum of the van der Waals radii (3.10 Å) of the atoms concerned²⁸ and the existence of a Pd—O bond is supported by NMR studies (vide infra). Similar types of apical Pd—O interactions have been observed in other Pd(II) complexes and are significantly longer than those in basal sites of square pyramidal coordination spheres. For example, the axial Pd—O bond distance in [Pd-([15]aneN₂OS₂)] is 2.779(4) Å,²⁹ and for [Pd(hfac)₂{P(*o*-tolyl)₃}]³⁰ and [Pd(hfac)(triphos)]³¹ it is 2.797(6) and 2.653(6) Å, respectively. In contrast, Pd—O lengths in equatorial sites are 2.110(3) Å for [Pd(F₆acac)₂(triphos)]³¹ and 1.98 Å (average length) for planar *cis*-[Pd{PhC(O)CHC(O)Me}₂].^{32,33}

It is notable that the [234] ring conformation is found in [Pd(L)Cl₂] (torsion angles are presented in Table 3) whereas the [333] conformation dominates other [9]aneX₃ (X = N,S) complexes.³⁴ For all S—N mixed donor [9]aneX₃ ligands in their free forms, molecular mechanics simulations indicate that [234] conformations are more strained than [333] by about 12–20 kJ mol⁻¹.^{34,35}

The structure of [Cu(L)₂]⁺ is shown in Figure 2. Selected bond lengths and angles are presented in Table 4. The copper(I) in [Cu(L)₂]⁺ is coordinated by two pairs of sulfur atoms

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Table 4. Selected Bond Distances and Angles in $[\text{Cu}(\text{L})_2][\text{ClO}_4]\cdot\text{CH}_3\text{CN}$

Distances (Å)			
Cu—S(1)	2.302(1)	Cu—S(4)	2.345(1)
Cu—S(2)	2.356(1)	Cu—S(3)	2.292(1)
Angles (deg)			
S(1)—Cu—S(2)	92.99(4)	S(1)—Cu—S(3)	130.20(5)
S(1)—Cu—S(4)	115.10(4)	S(2)—Cu—S(3)	119.86(5)
S(2)—Cu—S(4)	103.88(4)	S(3)—Cu—S(4)	93.53(4)

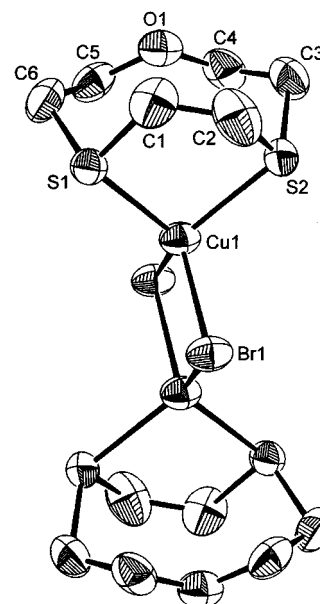
Table 5. Torsion Angles (deg) in $[\text{Cu}(\text{L})_2]^+$

S(3)—C(7)—C(8)—S(4)	-46.3(4)
S(4)—C(9)—C(10)—O(2)	-66.9(4)
S(1)—C(1)—C(2)—S(2)	-49.5(4)
S(1)—C(6)—C(5)—O(1)	60.8(4)
C(2)—C(1)—S(1)—C(6)	129.8(3)
C(4)—O(1)—C(5)—C(6)	-141.4(4)
C(7)—C(8)—S(4)—C(9)	-70.0(4)
S(2)—C(3)—C(4)—O(1)	-68.5(4)
C(9)—C(10)—O(2)—C(11)	137.5(4)
S(3)—C(12)—C(11)—O(2)	58.0(4)
C(1)—S(1)—C(6)—C(5)	-76.9(3)
C(1)—C(2)—S(2)—C(3)	-68.2(3)
C(2)—S(2)—C(3)—C(4)	97.1(3)
C(3)—C(4)—O(1)—C(5)	134.2(4)
C(7)—S(3)—C(12)—C(11)	-77.0(4)
C(8)—S(4)—C(9)—C(10)	94.7(4)
C(8)—C(7)—S(3)—C(12)	128.7(3)
C(10)—O(2)—C(11)—C(12)	-141.5(4)

from two ligand molecules so that the coordination geometry about copper is tetrahedral. The Cu—S distances range from 2.292(1) to 2.345(1) Å, with an average length of 2.324 Å. These may be compared to those in $[\text{Cu}(\text{L}')_2]^+$ ($\text{L}' = 2,5,8$ -trithia[9]-(2,5)thiophenophane)³⁶ which range from 2.301(3) to 2.392(3) Å, with an average of 2.340 Å. The angles about copper in $[\text{Cu}(\text{L})_2]^+$ vary from 92.99(4) to 130.20(5)°. The distortions from ideal tetrahedral angles arise mainly from constraints within the macrocyclic rings. When two coordinated sulfur atoms are from the same ligand, the S—Cu—S angle is compressed to about 93°, as is often found in five-membered chelate rings involving copper.^{36–38} When the sulfur atoms are in different ligand molecules, the S—Cu—S angles are larger with one being as large as 130.20(5)°.

The [2+2] coordination by the two ligands in $[\text{Cu}(\text{L})_2]^+$ is different from that found in $[\text{Cu}(\text{9}]\text{aneS}_3)_2]^+$, which has [3+1] coordination.³⁹ This difference can be attributed in part to the preference of copper(I) for soft S donors over hard O donors, so L is not constrained to adopt facial coordination as [9]aneS₃ does. Thus, L in $[\text{Cu}(\text{L})_2]^+$ has a conformation with lone pairs of its thioether sulfurs being in endo orientations and coordinated to copper but the lone pairs of the ether oxygen, although also endo, lie on the opposite side of the ring and are therefore unable to coordinate to copper. Since this conformation differs from that found in $[\text{Pd}(\text{L})\text{Cl}_2]$ (vide supra), L would seem to be a rather flexible ligand. Torsion angles for $[\text{Cu}(\text{L})_2]^+$ are given in Table 5.

The structure of $[\text{Cu}(\text{L})\text{Br}_2]$ is illustrated in Figure 3. Selected bond lengths and angles are presented in Table 6. The molecule of $[\text{Cu}(\text{L})\text{Br}_2]$ is a centrosymmetric dimer with two copper(I) centers in tetrahedral coordination linked by two inequivalent bromine bridges (Cu—Br = 2.557(1) Å and Cu—Br' = 2.392-

**Figure 3.** ORTEP of $[\text{Cu}(\text{L})\text{Br}_2]$. Thermal ellipsoids are shown at the 50% probability level.**Table 6.** Selected Bond Distances and Angles in $[\text{Cu}(\text{L})\text{Br}_2]$

Distances (Å)			
Br(1)—Cu	2.557(1)	Br(1)*—Cu	2.392(1)
Cu—S(1)	2.338(2)	Cu—S(2)	2.345(1)
Angles (deg)			
Cu—Br(1)—Cu*	70.28(4)	Br(1)—Cu—Br(1)*	109.72(4)
Br(1)—Cu—S(1)	104.22(5)	Br(1)—Cu—S(2)	99.34(5)
Br(1)—Cu—S(1)	120.55(5)	Br(1)—Cu—S(2)	126.47(4)
S(1)—Cu—S(2)	92.76(6)		

(1) Å). The copper atoms are, in addition, each bonded to two sulfur donors from one macrocyclic ligand (Cu—S = 2.338(2) Å and 2.345(1) Å). Bond angles around copper deviate from perfect tetrahedral geometry and range from 92.76(6) to 126.47(4)°. The smallest is the S—Cu—S angle associated with the chelate ring, and the largest is Br(1)—Cu—S(2) involving the longer Cu—Br bond. The Cu—Cu distance is 2.852(1) Å, and the Cu—Br—Cu' angle is 70.28(4)°. This Cu—Cu distance is shorter than those in $(\text{NEt}_4)_2[\text{Cu}_2\text{Br}_4]$ (2.937(3) Å)⁴⁰ and $[\text{Cu}_2(\text{triphenylphosphine})_3\text{Br}_2]$ (2.992(2) Å)⁴¹ but longer than that in $[(\text{AsPh}_3)(\text{MeCN})\text{Cu}]_2$ (2.779(1) Å).⁴² Mehrotra and Hoffmann⁴³ have suggested that a Cu—Cu distance of 2.83 Å represents overlap populations of 0.32 (bonding energy -0.417 eV) from molecular orbital calculations on tetrameric Cu_4^{4+} clusters. Thus, there may be a weak copper—copper interaction in $[\text{Cu}(\text{L})\text{Br}_2]$. The conformation of the ligand in this compound is similar to that in $[\text{Cu}(\text{L})_2]^+$.

The structure of $[\text{Co}(\text{L})_2]^{2+}$ is illustrated in Figure 4, and selected bond lengths and angles are presented in Table 7. The cation is centrosymmetric with a pseudooctahedral coordination sphere and only minor distortions from regular geometry. The Co—S (2.246(2) and 2.249(2) Å) distances of low-spin (vide infra) $[\text{Co}(\text{L})_2]^{2+}$ are roughly similar to those in $[\text{Co}(\text{L}'')_2]^{2+}$ ($\text{L}'' = [10]\text{aneS}_3$)⁴⁴ of 2.320(3), 2.257(3), and 2.395(3) Å, the longest in the L'' complex being the result of Jahn—Teller distortion. The Co—O (2.235(6) Å) distances in $[\text{Co}(\text{L})_2]^{2+}$ are significantly greater than those in high-spin $[\text{Co}(\text{20}]\text{aneO}_2\text{S}_4)]^{2+}$

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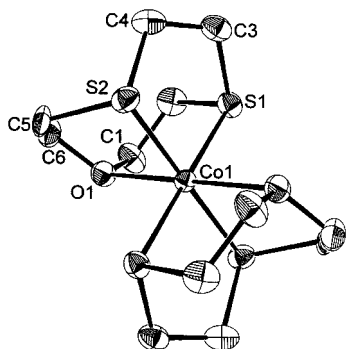


Figure 4. ORTEP of $[\text{Co}(\text{L})_2]^{2+}$. Thermal ellipsoids are shown at the 50% probability level.

Table 7. Selected Bond Distances and Angles in $[\text{Co}(\text{L})_2][\text{ClO}_4]_2 \cdot 2\text{CH}_3\text{NO}_2$

Distances (Å)			
Co–S(1)	2.246(2)	Co–S(2)	2.249(2)
Co–O(1)	2.235(6)		
Angles (deg)			
S(1)–Co–S(2)*	89.51(8)	S(1)–Co–S(2)	90.49(8)
S(1)–Co–O(1)	84.7(2)	S(1)*–Co–O(1)	95.3(2)
S(2)–Co–O(1)	83.3(2)	S(2)–Co–O(1)*	96.66(6)
S(1)–Co–S(1)*	95.29(6)		

Table 8. Torsion Angles (deg) in $[\text{Co}(\text{L})_2]^{2+}$

C(1)–O(1)–C(6)–C(5)	–146.7(8)
C(1)–C(2)–S(1)–C(3)	–124.1(7)
C(2)–S(1)–C(3)–C(4)	63.1(7)
C(2)–C(1)–O(1)–C(6)	75.2(9)
C(3)–C(4)–S(2)–C(5)	–129.7(7)
C(4)–S(2)–C(5)–C(6)	61.2(7)
S(1)–C(2)–C(1)–O(1)	49.6(9)
S(1)–C(3)–C(4)–S(2)	47.2(8)
S(2)–C(5)–C(6)–O(1)	47.7(9)

(2.098(6) Å),¹⁴ which has the same donors but in a 20-membered macrocyclic ring. The increase in $[\text{Co}(\text{L})_2]^{2+}$ is due to Jahn–Teller distortion that is not present in the high-spin complex. Interestingly, the Co–S bonds (2.444(2) Å) in high-spin $[\text{Co}(\text{[20]aneO}_2\text{S}_4)]^{2+}$ are significantly longer than those in low-spin $[\text{Co}(\text{L})_2]^{2+}$, which has the same S_4O_2 donor set. The difference may be related to spin state since the high-spin system has a lower population of its bonding t_{2g} orbitals and a higher occupancy of its antibonding e_g^* orbitals that arise from the π -acid nature of the thioether ligands.^{15,45,46} The conformation of the ligand in this complex is [333], like that in most [9]-aneX₃ (X = N, S) complexes³⁴ but unlike that in the other complexes in this report, again indicating the flexibility of the ligand. Selected torsion angles are given in Table 8.

The ¹H NMR spectrum of $[\text{Pd}(\text{L})\text{Cl}_2]$ in nitrobenzene-*d*₅ at room temperature is shown in Figure 5. The spectrum is consistent with the structure in Figure 1, which contains 12 NMR-nonequivalent hydrogens. These hydrogens present three ABCD patterns, of which two are overlapping. Resonances in the range 4.61–4.91 ppm are due to the four hydrogens of the coordinated $-\text{CH}_2\text{OCH}_2-$ group and are at lower field than corresponding resonances of the free ligand (3.95 ppm). Signals from two of four hydrogens in the $-\text{SCH}_2\text{CH}_2\text{S}-$ unit appear in the 3.5–3.7 ppm range, while the other two hydrogens have signals that overlap in the area of 3.3–3.5 ppm with those from two hydrogen atoms of the $-\text{CH}_2\text{SC}_2\text{H}_4\text{SCH}_2-$ group. The signals at 2.9–3.1 ppm are due to the remaining pair of

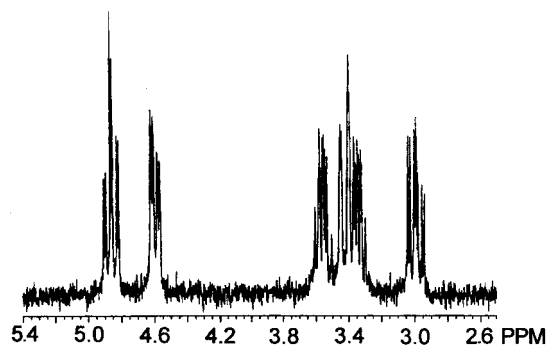


Figure 5. ¹H NMR of $[\text{Pd}(\text{L})\text{Cl}_2]$ in nitrobenzene-*d*₅ at room temperature.

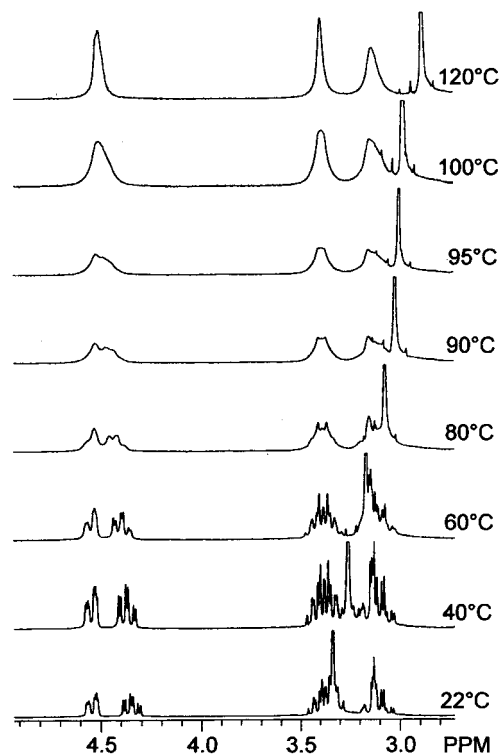


Figure 6. ¹H NMR of $[\text{Pd}(\text{L})\text{Cl}_2]$ in dimethyl-*d*₆ sulfoxide at various temperatures.

hydrogen atoms in the $-\text{CH}_2\text{SC}_2\text{H}_4\text{SCH}_2-$ group. Raising the temperature to 140 °C causes no change in the spectrum, indicating that the structure is quite rigid in nitrobenzene.

In dimethyl sulfoxide (DMSO), however (Figure 6), raising the temperature from 22 to 120 °C causes the two $-\text{CH}_2\text{O}-$ signals to coalesce to a single broad band, while peaks in the $-\text{SCH}_2\text{CH}_2\text{S}-$ and $-\text{CH}_2\text{C}_2\text{H}_4\text{SCH}_2-$ regions also merge into two broad resonances. These differing observations in nitrobenzene and dimethyl sulfoxide suggest a solvent-induced process is occurring in DMSO. To determine whether that process is dissociative or nondissociative, free ligand was added to solutions of the complex. Upon warming, free-ligand resonances (at 2.79, 3.07, and 3.94 ppm) broaden and collapse at the same rate as do the signals from the coordinated ligand, suggesting that a ligand exchange process is involved. The nature and role of the solvent in this process are critical since the temperature dependence of the spectrum is not observed in nitrobenzene. In fact, addition of as little as 10% by volume DMSO to the nitrobenzene solutions quenches all fine structure in the spectrum measured at 120 °C.

Cyclic voltammetry of $[\text{Cu}(\text{L})_2][\text{ClO}_4]$ in CH_3CN reveals a quasi-reversible one-electron wave at $E_{1/2} = 0.607$ V vs SCE with $\Delta E_p = 114$ mV at a scan rate of 110 mV/s. This wave

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becomes more irreversible as the scan rate is increased, but at all reasonable scan rates $i_p^a/i_p^c \approx 1$. The ligand is electrochemically silent in the potential range 0–1000 mV vs SCE. Corresponding parameters for $[\text{Cu}(\text{[9]aneS}_3)_2]^{2+}$ (S_6 in two rings) and $[\text{Cu}(\text{[18]aneS}_6)]^{2+}$ (S_6 in one ring) are $E_{1/2} = 0.61$ and 0.72 V vs SCE and $\Delta E_p = 90$ and 110 mV, respectively.⁴⁷ This seems to indicate that the [2+2] coordination of L in $[\text{Cu}(\text{L})_2]^+$ that provides an S_4 coordination sphere to Cu(I) stabilizes Cu(I) just as well as the [3+1] S_4 donor set in $[\text{Cu}(\text{[9]aneS}_3)_2]^+$ and moreover a similar situation applies with respect to Cu(II). In the first instance, the Cu(II) situation seems difficult to understand when the donor set is $2 \times S_3$ in one case and $2 \times S_2O$ in the other. However, the expected Jahn–Teller distortion in Cu(II) pseudooctahedral species, which is quite apparent in the structure of $[\text{Cu}(\text{[18]aneS}_6)]^{2+}$,⁴⁷ may well give an effective ligand field of S_4 in both cases with the influence of the additional two S or O donors being sufficiently weak to be of no great electrochemical significance.

The comparatively large value of ΔE_p for $[\text{Cu}(\text{L})_2]^+$ (114 mV) and its increase with scan speed are similar to the behavior of $[\text{Cu}(\text{[9]aneS}_3)_2]^+$ ³⁹ and, as for that ion, may be attributed here also to the conformational and structural changes that follow the relatively more rapid electron transfer step in the redox process.

For $[\text{Cu}(\text{L})\text{Br}]_2$ in acetonitrile, there is a single quasi-reversible wave with $E_{1/2} = 0.594$ V and $\Delta E_p = 107$ mV at scan speeds in the range 40–160 mV/s. The potential of this wave is not greatly different from that observed for $[\text{Cu}(\text{L})_2]^+$, but the process is marginally more reversible, as indicated by a slightly smaller ΔE_p and by the lack of change in ΔE_p with scan rate. It is perhaps surprising that there should be so little change in $E_{1/2}$ between these two copper complexes in spite of significant differences in their coordination spheres. It is known, however, that related complexes undergo partial solvolysis with loss of halide ligands,⁴⁸ and it may be that the actual solution structures of these two complexes are more closely related than their solid state structures would suggest.

The magnetic susceptibility of $[\text{Co}(\text{L})_2][\text{ClO}_4]_2$ as a function of temperature is typical of a magnetically dilute species, and μ_{eff} only varies from 1.74 to $2.04 \mu_B$ over the entire temperature range 5–292 K. The value of μ_{eff} clearly indicates a low-spin Co(II) system, an observation that is interesting in view of the fact that $[\text{Co}(\text{[20]aneS}_4\text{O}_2)]^{2+}$, which has the same donor set but in one instead of two rings, is high spin with $\mu_{\text{eff}} = 4.37 \mu_B$ at 22 °C. Perhaps this is not surprising, since both $[\text{Co}(\text{L}_2)]^{2+}$

($\text{L}_2 = 1,4,7$ -trithiadecan-9-ol),¹⁴ which has a $2 \times S_3$ donor set, and $[\text{Co}(\text{L}_3)]^{2+}$ ($\text{L}_3 = 1,12$ -bis(2-pyridyl)-2,5,8,11-tetrathia-dodecane),⁴⁹ which has an N_2S_4 donor set, exhibit spin-crossover behavior, which could be construed to suggest that Co(II), in presence of four or more thioether donors, is “electronically fragile” with respect to its spin state.

Conclusions

The coordination behavior of 1-oxa-4,7-dithiacyclononane is similar in many respects to that of 7-aza-1,4-dithiacyclononane and related ligands that provide N_2S_4 donor sets whether in one ring or two.^{6,8,9} Thus, the flexibility of 1-oxa-4,7-dithiacyclononane (ligand L), expressed as different conformations in different complexes, parallels the experience with 7-aza-1,4-dithiacyclononane. Although macrocyclic polythioethers often engage in binding site fluxionality,^{17,50} the introduction of an oxygen atom precludes this activity and leads to rigid complexes except when nucleophilic solvent intervention leads to dissociative equilibria involving free and complexed ligands. The cyclic voltammetric behavior of the two copper complexes of L investigated in this study is remarkably similar to that of their 1,4,7-trithiacyclononane analogs in spite of the structural differences between the ligands. The ligand field provided by the thioether/ether combination of donors in L gives a uniformly low-spin Co(II) complex in the temperature range 5–292 K, in contrast to $[\text{Co}(\text{[20]aneS}_4\text{O}_2)]^{2+}$, which is high spin at room temperature in spite of having the same coordination sphere donor set. This suggests subtle structural effects influence the high-spin/low-spin crossover in such compounds.

Acknowledgment. Financial support from the Natural Sciences and Engineering Research Council of Canada and Memorial University of Newfoundland is acknowledged. The assistance of Dr. L. K. Thompson with the variable-temperature magnetic susceptibility measurements is gratefully acknowledged.

Supporting Information Available: A description of the X-ray studies and tables of positional parameters and equivalent isotropic temperature factors, bond lengths, bond angles, anisotropic thermal parameters and hydrogen atom locations (28 pages). Ordering information is given on any current masthead page.

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