Inorg. Chem. **1989**, *28*, 4593–4598 **4593**

Chart II

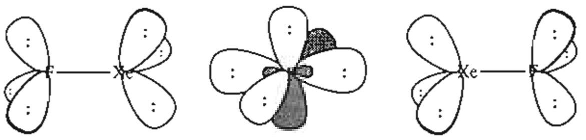
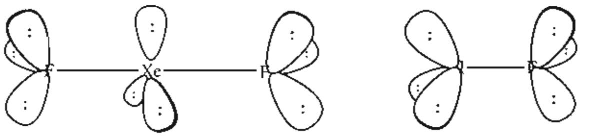


Chart III



lone pairs on each of the terminal fluorines that are bent away from the σ bond and the Xe. There are three lone pairs on each Xe bent away from the σ bond and F_T toward F_c. There are two Xe–F_T σ bonds that have centroids closer to the F_T than to Xe. The remaining four valence orbitals are predominantly on F_c. There are two lone pairs that are $sp^{3.5}$ hybrids approximately perpendicular to each other and to the molecular axis. The remaining two orbitals are similar to lone pairs on F_c that are delocalized onto the xenons by 0.10–0.12e. The orbitals bend away from the molecular axis and have hybridizations of $sp^{2.41}$ and $sp^{2.56}$. The Boys LMO criteria is known to be biased against σ–π (s–p) separation because it tries to have maximum separation of the centroids of charge for each orbital. The 5c,6e hypervalent bond for this system has s–p separation in that the hypervalent bond is composed of p orbitals (σ_2 in Figure 1A has only 0.03e in the 2s on F_c) and does not include the 2s orbital on F_c. Thus, the centroids of charge of the p orbital (on F_c involved in the σ bond) and the 2s orbital are identical. The Boys criteria tries to maximally separate these centroids. However, this is difficult, leading to very poor convergence.

For $XeIF_3$, there are no symmetry constraints as in $[Xe_2F_3]^+$ on σ–π separation and the localization converges quickly. There are three lone pairs on each atom and there are three σ bonds, I–F_T, Xe–F_T and Xe–F_c (Chart III). Thus the LMO's for $XeIF_3$ do not show any of the bonding found in our analysis of the hypervalent 5c,6e bond based on the canonical MO's.

Conclusions

The analysis of the canonical molecular orbitals clearly shows the presence of a 5c,6e hypervalent bond in $[Xe_2F_3]^+$. The atomic charges are also consistent with such a description. The LMO's on the other hand do not show such a description well precisely because they are localized. The hypervalent 5c,6e bond requires delocalization over five centers. Furthermore, there are only three electron pairs to distribute over four bonding interatomic regions. Thus the LMO's converge poorly and prefer a picture more consistent with a fully ionic model, i.e., an F^- binding two $[Xe–F]^+$ fragments. However, the LMO's do try to make weak σ bonds between F_c and the Xe's consistent with the hypervalent model. For $XeIF_3$, the description of the bonding is more complex. The highest occupied σ_4 orbital clearly has a 5c,6e hypervalent bond component as does the σ_3 orbital. However, the bonding σ_2 and σ_1 orbitals are more like those of the fragment molecules XeF_2 and IF, especially with the mixing of the fluorine p with the valence s on iodine as found in σ_1. With this behavior of σ_1 and σ_2 for the canonical molecular orbitals, it is not surprising that the LMO's are essentially those of the isolated fragments. However, the calculated geometry, vibrational spectra, and energetics for $XeIF_3$ are consistent with more than weakly interacting fragments and there is some component of a hypervalent bond.

Registry No. $[Xe_2F_3]^+$, 37366-73-7; $[XeIF_3]$, 123148-33-4; XeF_2, 64054-70-2; IF, 13873-84-2; $[XeF]^+$, 47936-70-9; $[IF_2]^-$, 25730-98-7.

Supplementary Material Available: A table of molecular coordinates and LMO centroids of charge for $[Xe_2F_3]^+$ and $XeIF_3$ (2 pages). Ordering information is given on any current masthead page.

Contribution from the Dipartimento di Scienze Chimiche and Istituto Chimico, Facoltà di Ingegneria,
Università di Catania, 95125 Catania, Italy, and Department of Chemistry,
Louisiana State University, Baton Rouge, Louisiana 70803-1804

Preparation, Characterization, and Structural Aspects of Transition-Metal Complexes with 4,7,10-Trioxa-1,13-dithia[13](2,5)-1,3,4-thiadiazolophane

Raffaele Bonomo,[†] Francesco Bottino,[†] Frank R. Fronczek,[‡] Antonino Mamo,[§]
and Sebastiano Pappalardo*[,†]

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The title compound **5** readily forms discrete 2:1 (ligand to metal) complexes with Cu(II), Co(II), and Ni(II) nitrates and with $CuBr_2$ and a highly crystalline polymeric 2:3 (ligand to metal) complex with $CdCl_2$. The complexes have been characterized by chemical analysis, FAB mass spectrometry, ^{1}H NMR spectroscopy (for the diamagnetic Cd(II) complex **10**), electronic spectral studies, and EPR spectroscopy. Structures of the free ligand and its complexes with $CuBr_2$ and $CdCl_2$ have also been determined. X-ray crystal structure determinations have shown that the macrocyclic ligand does not accommodate the metal ions inside the cavity but rather coordinates on the exterior through a nitrogen atom(s). The heterocyclic ring acts as a monodentate ligand in the trans square-planar Cu(II) complex **9** and as a bridging bidentate ligand in the octahedral Cd(II) complex **10**. Cd atoms in **10** are linked through bis(μ-chloro) bridges into infinite chains, the macrocyclic units serving as bridging ligands through the two nitrogen atoms. $C_{10}H_{16}N_2O_3S_3$ (**5**) is tetragonal, $P4_12_12$ (or $P4_32_12$), with $a = 9.3369$ (11) Å, $c = 15.761$ (2) Å, $Z = 4$, and $R = 0.027$ for 1653 observations. $CuBr_2(C_{10}H_{16}N_2O_3S_3)_2$ (**9**) is triclinic, $P\bar{1}$, with $a = 8.3452$ (13) Å, $b = 9.2414$ (10) Å, $c = 11.7586$ (8) Å, $\alpha = 71.313$ (7)°, $\beta = 78.347$ (9)°, $\gamma = 63.120$ (12)°, $Z = 1$, and $R = 0.043$ for 3033 observations. $Cd_3Cl_6(C_{10}H_{16}N_2O_3S_3)_2\cdot 2CH_3OH$ (**10**) is triclinic, $P\bar{1}$, with $a = 10.133$ (3) Å, $b = 10.187$ (2) Å, $c = 11.740$ (2) Å, $\alpha = 72.834$ (11)°, $\beta = 68.327$ (15)°, $\gamma = 63.52$ (2)°, $Z = 1$, and $R = 0.020$ for 3206 observations.

Introduction

Various 1,3,4-thiadiazole sulfur derivatives are well-known for their ability to form stable complexes with heavy- and transition-metal ions.[1] 2,5-Dimercapto-1,3,4-thiadiazole (**1**, Bismuthiol I) is among the most extensively studied ligands of this class[2] and has found application as an analytical reagent in the detection and determination of metal ions,[3] and its complexes have industrial

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[†] Dipartimento di Scienze Chimiche, Università di Catania.
[‡] Louisiana State University.
[§] Istituto Chimico, Facoltà di Ingegneria, Università di Catania.

(1) Sandström, J. *Adv. Heterocycl. Chem.* **1968**, *9*, 165.
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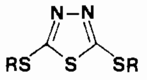
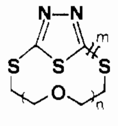
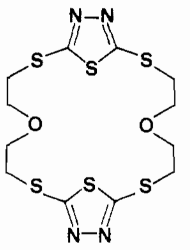


1 R = H

2 R = alkyl



3



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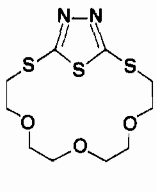

5

importance or show interesting pharmacological properties.[2c,4] Several transition-metal complexes with 2,5-bis(alkylthio)-1,3,4-thiadiazoles (**2**; R = methyl, *tert*-octyl) have been also reported,[5] but little work has been done on the determination of their structures. Depending on the metal used, different stoichiometries of the complexes have been observed, and the ligands have been proposed (on the basis of IR and electronic spectral studies) to coordinate with one and/or both endocyclic nitrogen atoms[5c,d] or with one nitrogen atom and one exocyclic sulfur atom.[5b]

As part of a program directed toward the synthesis and ion binding properties of multidentate macrocyclic compounds containing 2,5-dithio-1,3,4-thiadiazole moieties,[6] a variety of 1,3,4-thiadiazolo thia crown ethers (**3**; $m = 1$–4; $n = 1$–3) with differing ring sizes and flexibilities have recently been synthesized as potential ligands for the complexation of transition-metal ions.[7] In order to evaluate the chelating tendencies of this new class of multidentate macrocyclic ligands, some transition-metal complexes have been prepared, and extensive X-ray structural investigations have been conducted to afford precise insight into their geometries and modes of binding sites.

In a previous paper we have described the crystal structures of the 2:2 macrocycle 4,16-dioxa-1,7,13,19-tetrathia[7.7](2,5)-1,3,4-thiadiazolophane[8] (**4**) and its complex with $Cu(NO_3)_2$.[9] We found that the macrocyclic ligand does not encapsulate a Cu(II) ion to form a discrete 1:1 complex but rather coordinates externally through nitrogen atoms to afford linear polymeric complexes. We report now the preparation, characterization, and structural aspects of Cu(II), Co(II), Ni(II), and Cd(II) complexes with the 1:1 macrocycle 4,7,10-trioxa-1,13-dithia[13](2,5)-1,3,4-thiadiazolophane (**5**).

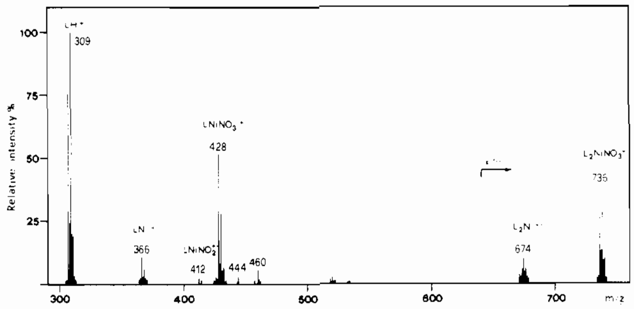

Figure 1. Positive ion FAB mass spectrum of the Ni(II) complex **8**.

Experimental Section

General Comments. Melting points were determined on a Kofler apparatus and are uncorrected. Elemental analyses were obtained commercially. Positive ion FAB mass spectra were recorded on a Kratos MS 50 double-focusing mass spectrometer, equipped with a standard FAB source, using 3-nitrobenzyl alcohol as a matrix. ^1H NMR spectra were measured on a Bruker AC 250 spectrometer using CD_3OD as solvent, with Me_4Si as the internal standard. Electronic spectra were taken on a Perkin-Elmer 330 double-beam spectrophotometer using 10^{-2}–10^{-3} M acetonitrile solutions at room temperature. EPR spectra were recorded with a conventional X-band spectrometer (Bruker ER 200 D), equipped with a low-temperature control unit. DPPH ($g = 2.0036$) was used to calibrate the klystron frequency, the magnetic field being continously measured by means of a Model ER 035 M gauss meter, which gives markers at preselected values. EPR spectra were run at 150 K.

$Cu(NO_3)_2\cdot 3H_2O$, $Co(NO_3)_2\cdot 6H_2O$, and $Ni(NO_3)_2\cdot 6H_2O$ were dried in vacuo (1 mmHg) for 24 h before use. $CuBr_2$ was recrystallized from absolute methanol, while anhydrous $CdCl_2$ was obtained from $CdCl_2\cdot 2H_2O$ by refluxing in triethyl orthoformate for several hours. The macrocyclic ligand **5** was available from a previous work.[7]

Complexes of 5 with Cu(II), Co(II), Ni(II), and Cd(II). General Procedure. To a stirred solution of **5** (154 mg, 0.5 mmol) in warm absolute MeOH (5 mL) was added a solution of the metal salt (0.5 mmol) in warm MeOH (5 mL). The mixture was refluxed for 1 h. After evaporation of the solvent in vacuo, the residue was washed with diethyl ether and then crystallized from an appropriate solvent to afford the desired complex in 70–80% yield. The physicochemical characteristics of the complexes are summarized in Table I.

Crystal Structure Determinations. Intensity data were collected on Enraf-Nonius CAD-4 diffractometers equipped with Mo Kα ($\lambda = 0.71073$ Å) or Cu Kα ($\lambda = 1.54184$ Å) radiation and graphite monochromators. The ω–2θ scans were made at variable rates designed to yield equal relative precision for observable intensities. Crystal data and specifics of data collection are given in Table II. Data reduction included corrections for background, Lorentz, polarization, and absorption effects, the last based on ψ scans. No intensity decay occurred during any of the data collections. Redundant data for the uncomplexed ligand data set were averaged. Reflections having $I > 3\sigma(I)$ were considered observed and were used in the refinements.

The structure of the uncomplexed ligand was solved by direct methods; the two metal complex structures were solved by heavy-atom methods. Structures were refined by full-matrix least squares based on F with weights $w = \sigma^{-2}(F_o)$, with use of the Enraf-Nonius SDP programs,[10] the scattering factors of Cromer and Waber,[11] and the anomalous coefficients of Cromer.[12] Non-hydrogen atoms were treated anisotropically; hydrogen atoms were located from difference maps and treated as specified in Table II. Secondary extinction parameters were refined for all three structures, and their final values, as well as R factors and residual electron densities, are also given in Table II. An attempt to determine the

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Table I. Physicochemical and Analytical Data for Transition-Metal Complexes **6–10**

metal salt	complex	composition	color	mp, °C (crystallizn solvent)	anal. data found (calcd) % C	% H	% N
$Cu(NO_3)_2 \cdot 3H_2O$	**6**	$L_2Cu(NO_3)_2$	green	154–156 (CH_3CN)	29.49 (29.86)	3.94 (4.01)	10.22 (10.45)
$Co(NO_3)_2 \cdot 6H_2O$	**7**	$L_2Co(NO_3)_2$	purple	164–165 (CH_3COCH_3)	29.85 (30.03)	4.01 (4.03)	10.54 (10.51)
$Ni(NO_3)_2 \cdot 6H_2O$	**8**	$L_2Ni(NO_3)_2$	emerald green	191–193 (CH_3CN)	29.63 (30.01)	3.67 (4.03)	10.34 (10.51)
$CuBr_2$	**9**	L_2CuBr_2	brown	162–164 (CH_3OH)	28.73 (28.59)	3.72 (3.84)	7.23 (6.67)
$CdCl_2$	**10**	$L_2(CdCl_2)_3 \cdot 2CH_3OH$	white	>275 (CH_3OH)	20.76 (21.47)	3.14 (3.27)	4.45 (4.55)

Table II. Crystallographic Data for **5**, **9**, and **10**

	5	**9**	**10**
formula	$C_{10}H_{16}N_2O_3S_3$	$CuBr_2(C_{10}H_{16}N_2O_3S_3)_2$	$Cd_3Cl_6(C_{10}H_{16}N_2O_3S_3)_2 \cdot 2CH_3OH$
fw	308.4	840.2	1230.9
cryst syst	tetragonal	triclinic	triclinic
space group	$P4_12_12$ (or $P4_32_12$)	$P\bar{1}$	$P\bar{1}$
a, Å	9.3369 (11)	8.3452 (13)	10.133 (3)
b, Å		9.2414 (10)	10.187 (2)
c, Å	15.761 (2)	11.7586 (8)	11.740 (2)
α, deg		71.313 (7)	72.834 (11)
β, deg		78.347 (9)	68.327 (15)
γ, deg		63.120 (12)	63.52 (2)
V, Å^3	1374.0 (5)	764.5 (2)	995.6 (4)
d, g cm^{-3}	1.491	1.825	2.053
Z	4	1	1
λ, Å	0.71073 (Mo Kα)	1.54184 (Cu Kα)	0.71073 (Mo Kα)
μ, cm^{-1}	5.2	82.5	23.4
T, °C	22	24	21
min transmissn, %	95.16	85.22	82.59
R	0.027	0.043	0.020
R_w	0.031	0.073	0.028

Table III. Coordinates of Non-Hydrogen Atoms for $C_{10}H_{16}N_2O_3S_3$ (**5**)[a]

atom	x	y	z
S1	0.91626 (4)	x	1
S2	0.80577 (5)	1.17651 (4)	0.89981 (3)
O1	0.6317 (1)	0.8771 (1)	0.92624 (6)
O2	0.5706 (1)	x	1
N	1.0597 (2)	1.1441 (2)	0.9744 (1)
C1	0.9376 (2)	1.0843 (2)	0.95634 (9)
C2	0.7353 (2)	1.0421 (2)	0.82749 (9)
C3	0.6016 (2)	0.9688 (2)	0.85684 (9)
C4	0.5057 (2)	0.8140 (2)	0.9604 (1)
C5	0.5445 (2)	0.7115 (2)	1.0300 (1)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

Table IV. Coordinates of Non-Hydrogen Atoms for $CuBr_2(C_{10}H_{16}N_2O_3S_3)_2$ (**9**)[a]

atom	x	y	z
Br	0.00631 (4)	0.14638 (4)	0.13006 (3)
Cu	0	0	0
S1	0.52797 (8)	0.00310 (7)	−0.19038 (7)
S2	0.44774 (9)	−0.29165 (8)	−0.02451 (7)
S3	0.35101 (9)	0.38207 (7)	−0.31056 (7)
O1	0.7398 (3)	−0.3281 (2)	−0.2396 (2)
O2	0.7937 (3)	−0.1040 (2)	−0.4675 (2)
O3	0.6337 (3)	0.2666 (3)	−0.5132 (2)
N1	0.2175 (3)	0.0298 (2)	−0.0975 (2)
N2	0.1920 (3)	0.1910 (3)	−0.1661 (2)
C1	0.3434 (3)	0.1955 (3)	−0.2170 (2)
C2	0.3836 (3)	−0.0812 (3)	−0.1020 (2)
C3	0.6921 (4)	−0.3718 (3)	−0.0252 (3)
C4	0.7967 (4)	−0.4472 (3)	−0.1270 (3)
C5	0.8648 (4)	−0.3789 (4)	−0.3342 (3)
C6	0.7958 (4)	−0.2621 (4)	−0.4557 (3)
C7	0.7319 (5)	0.0115 (4)	−0.5796 (3)
C8	0.7486 (5)	0.1712 (4)	−0.5954 (3)
C9	0.7108 (4)	0.2216 (4)	−0.4044 (3)
C10	0.5877 (4)	0.3404 (3)	−0.3276 (3)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

Table V. Coordinates of Non-Hydrogen Atoms for $Cd_3Cl_6(C_{10}H_{16}N_2O_3S_3)_2 \cdot 2CH_3OH$ (**10**)[a]

atom	x	y	z
Cd1	0	1	0
Cd2	−0.34366 (2)	0.94576 (2)	0.06871 (2)
Cl1	−0.15148 (7)	1.01049 (7)	−0.14097 (6)
Cl2	−0.24942 (7)	1.04465 (6)	0.18726 (6)
Cl3	−0.57112 (6)	1.19076 (6)	0.02466 (6)
S1	0.07497 (7)	0.46596 (7)	0.15860 (7)
S2	0.31338 (7)	0.60989 (7)	0.04039 (6)
S3	−0.26803 (7)	0.53050 (7)	0.21754 (7)
O1	0.4094 (2)	0.4341 (2)	0.3680 (2)
O2	0.1826 (2)	0.2723 (2)	0.4861 (2)
O3	−0.0669 (2)	0.3003 (2)	0.4030 (2)
N1	−0.1267 (2)	0.7197 (2)	0.1093 (2)
N2	0.0091 (2)	0.7406 (2)	0.0711 (2)
C1	0.1246 (3)	0.6183 (3)	0.0901 (2)
C2	−0.1106 (3)	0.5821 (3)	0.1581 (2)
C3	0.3509 (3)	0.5841 (3)	0.1861 (2)
C4	0.3737 (3)	0.4332 (3)	0.2621 (2)
C5	0.4143 (3)	0.3065 (3)	0.4600 (3)
C6	0.2613 (3)	0.3083 (3)	0.5439 (2)
C7	0.0352 (3)	0.2840 (3)	0.5653 (3)
C8	−0.0367 (3)	0.2180 (3)	0.5179 (3)
C9	−0.1691 (3)	0.2624 (3)	0.3752 (3)
C10	−0.1810 (3)	0.3296 (3)	0.2457 (3)
O1M	−0.5322 (2)	0.8913 (2)	0.2506 (2)
C1M	−0.6281 (4)	0.9987 (4)	0.3322 (3)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

absolute configuration of **5** by refinement in both enantiomorphic space groups was inconclusive, and coordinates are given relative to $P4_12_12$. Coordinates for the three structures are listed in Tables III–V.

Results and Discussion

Complex Formation and Characterization. The reaction of **5** with Cu(II), Co(II), and Ni(II) nitrates and with $CuBr_2$ in absolute MeOH produced the brilliantly colored complexes **6–9**, respectively, which displayed microanalytical data consistent with a 2:1 ligand-to-metal stoichiometry (Table I). Complexation of **5** with $Cd(NO_3)_2 \cdot 4H_2O$ under identical conditions gave a white deliquescent material from which the pure complex could not be obtained. However, substitution of anhydrous $CdCl_2$ for the nitrate salt afforded the white crystalline Cd(II) complex **10**, having the unusual composition shown in Table I.

Table VI. Selected Fragment Ions in the Positive Ion FAB Mass Spectra of Complexes **6**–**9**[a]

			ion assignt				
complex	M	X	$[L_2MX]^+$	$[L_2M]^{\bullet+}$	$[LMX]^+$	$[LM]^{\bullet+}$	$[LH]^+$
6	Cu	NO_3	741 (1.7) 743 (2.1) 745 (1.1)	679 (29) 681 (21) 683 (5.6)	433 (3.5) 435 (3.8) 437 (2)	371 (100) 373 (70) 375 (10)	309 (11)
7	Co	NO_3	737 (7)	675 (1)	429 (83)	367 (1.7)	309 (100)
8	Ni	NO_3	736 (3.8) 738 (2.8) 740 (1)	674 (1) 676 (0.6) 678 (0.2)	428 (51) 430 (28) 432 (6.5)	366 (11) 368 (6) 370 (1.6)	309 (100)
9	Cu	Br		679 (6.4) 681 (5.1) 683 (1.1)		371 (23) 373 (13) 375 (2)	309 (100)

[a] Relative intensities in parentheses.

A rapid structural characterization of complexes **6**–**9** was achieved by fast atom bombardment (FAB) mass spectrometry.[13,14] The positive ion FAB mass spectrum of the Ni(II) complex **8**, typical of this series, is reported in Figure 1. Although the parent peak is absent, it shows diagnostically important peaks at *m/z* 736/738, corresponding to $[L_2NiNO_3]^+$, where L stands for the ligand, which confirms the assigned stoichiometry. Fragment ions at *m/z* 674/676, 428/430, and 366/368 are also present, due to the sequential loss of a NO_3 group and/or L from the $[L_2NiNO_3]^+$ ion. The fragment ion $[LH]^+$ (*m/z* 309) is the base peak in the spectrum. Experimental and calculated isomer distributions showed good agreement. Complexes **6**, **7**, and **9** give similar positive ion FAB mass spectra, indicating that a uniform fragmentation pattern is operative. Selected fragment ions and their relative abundances are collected in Table VI.

A positive ion FAB mass spectrum for the Cd(II) complex **10** could not be obtained, owing to its polymeric nature. The diamagnetic Cd(II) complex was, however, amenable to ^1H NMR analysis. The ^1H NMR spectrum of uncomplexed macrocycle **5** in CD_3OD displayed two triplets at δ 3.34 and 3.81 ($J = 5.2$ Hz) for α- and β-methylenes and a complex multiplet (12 lines) centered at δ 3.57 for γ- and δ-methylenes, with an integrating ratio of 4:4:8, respectively. The ^1H NMR spectrum of Cd(II) complex **10** in the same solvent was almost superimposable with that of **5** and only differed in a much higher intensity of the central line of the triplet assigned to the α-methylenes, due to the presence of coordinated methanol in the complex and to its accidentally isochronous chemical shift. Consistent with the composition given for complex **10** (Table I) an integrating ratio of 7:4:8 was found. The ^1H NMR data clearly indicate that the polyether chain in the ligand is not affected by complex formation; this means that the Cd(II) ion is not coordinated inside the cavity of the macrocycle but on the exterior through nitrogen atoms.

In order to determine the salient structural features of the ligand and of its transition-metal complexes, single crystals of **5**–**10** were grown from various solvents; only **5**, **9**, and **10**, however, gave suitable crystals for an X-ray diffraction study. In the absence of structural data, the stereochemistry in solution of the nitrate complexes **6**–**8** was tentatively deduced from their electronic and EPR spectra.

Structure Descriptions. a. Uncomplexed Macrocycle 5. The molecule lies on a crystallographic 2-fold axis, with the heterocyclic S atom pointing toward the interior of the molecule, as shown in Figure 2. The thiadiazole ring is planar, with a maximum deviation of 0.004 (2) Å from the best plane, and sulfur atoms S2 lie ±0.137 (1) Å out of this plane. The N–N′ distance is 1.376 (2) Å, while the C–S distances are 1.725 (2) Å for S1 (endocyclic) and 1.747 (2) Å for S2 (exocyclic). The endocyclic bond angle C1–S1–C1′ is 87.06 (7)°. Attachment of the polyether chain to the heterocyclic ring forms torsion angles S1–C1–S2–C2 of −46.14 (12)°. No intermolecular distances less than 3.4 Å between non-hydrogen atoms exist.

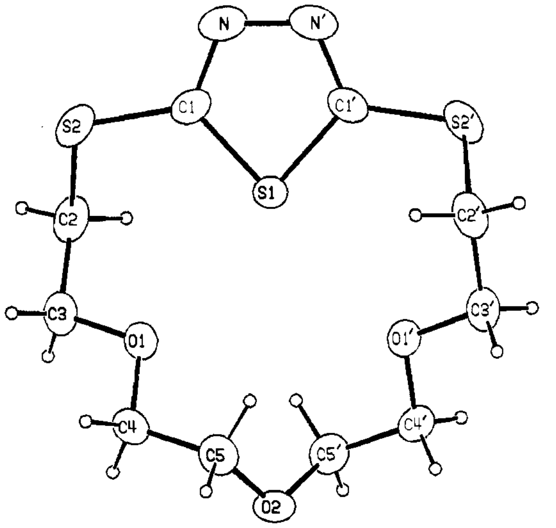

Figure 2. Molecular structure of the uncomplexed macrocycle **5**. The molecule lies on a crystallographic 2-fold axis, which relates atoms to their primed counterparts. Ellipsoids are drawn at the 40% probability level.

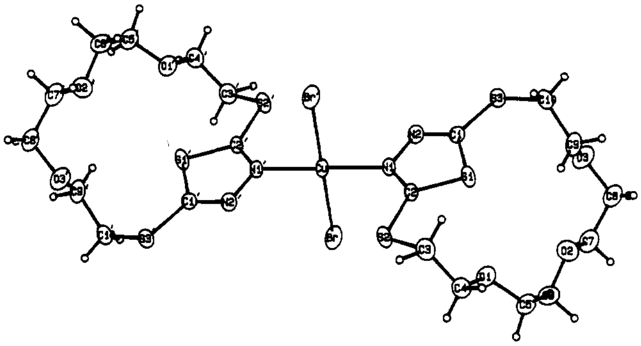

Figure 3. Molecular structure of the Cu(II) complex **9**. The Cu atom lies on a crystallographic inversion center, and primed atoms are related to unprimed atoms by that inversion. Ellipsoids are drawn at the 50% probability level.

b. Cu(II) Complex 9. The Cu(II) ion lies on a crystallographic center of symmetry and thus forms a trans planar complex, as shown in Figure 3. Coordination of the macrocyclic ligand is on the exterior, to a single N atom, with Cu–N1 distance 2.023 (1) Å, while the Cu–Br distance is 2.3652 (2) Å. The coordination is also very nearly square, as the Br–Cu–N1 angle is 89.79 (4)°. The thiadiazole ring is nearly planar, with a maximum deviation of 0.013 Å (for N2) from the best plane; the Cu atom lies slightly (0.125 (1) Å) out of this plane. The thiadiazole and coordination planes intersect with a dihedral angle of 71.33 (7)°. The geometry of the thiadiazole ring agrees well with that seen in the uncomplexed macrocycle: N–N = 1.388 (2) Å; C–N(av) = 1.300 (2) Å; C–S(av, endocyclic) = 1.726 (2) Å; C–S(av, exocyclic) = 1.741 (2) Å; C1–S1–C2 = 87.26 (8)°. Linkage of the polyether chain

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(13) Johnstone, R. A. W.; Rose, M. E. *J. Chem. Soc., Chem. Commun.* **1983**, 1268.

(14) Parker, D. *Org. Mass Spectrom.* **1985**, *20*, 260.

Table VII. Electronic and EPR Spectral Data for Transition-Metal Complexes **6**–**9**

complex	absorption bands $10^3\nu$, cm^{-1} (ϵ)			magnetic params			
				$g_\parallel$	$A_\parallel$, cm^{-1}	$g_\perp$	$A_\perp$, cm^{-1}
6		13.2 (40)		2.3797 (2)	0.0126 (2)	2.078 (5)	0.0015 (5)
7	8.1 (6)	19.3 (46)	21.2 (27)				
8	9.3 (7)	17.7 (13)	25.7 (30)				
9	15.8 (400)	20.8 (290)	23.2 (650)	2.317 (2)	0.0151 (2)	2.080 (5)	

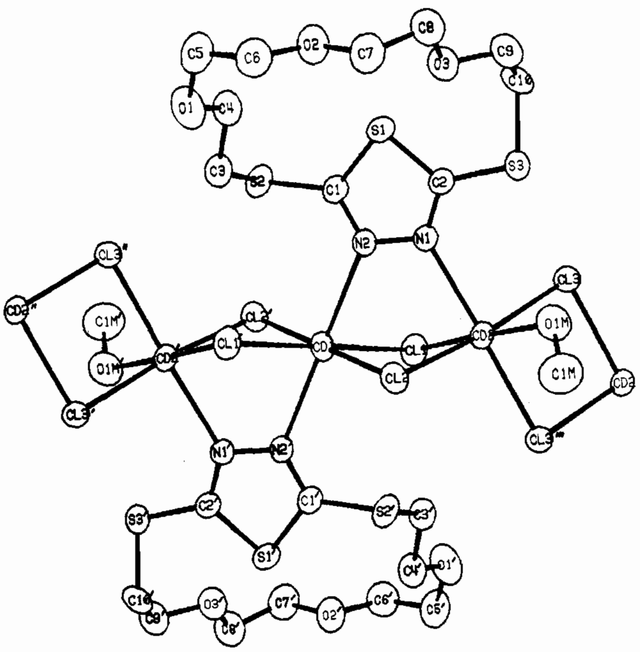

Figure 4. Portion of the chain structure of the Cd(II) complex **10**. Cd1 lies on a crystallographic inversion center, which relates unprimed atoms to those with single primes. Inversion centers also lie between pairs of Cd2 atoms. Ellipsoids are drawn at the 65% probability level.

to the heterocycle is much more nearly syn to the central S atom: torsion angles are S1–C1–S3–C10 = −17.8 (2)° and S1–C2–S2–C3 = 16.0 (2)°, and the macrocycle exhibits large deviations from the C_2 symmetry of the uncomplexed form. The thermal motion of the polyether chain is unexpectedly small, with equivalent isotropic thermal parameters in the range 1.8–3.5 Å^2 for C and O atoms. This macrocyclic conformation apparently allows efficient packing and precludes disorder and high thermal motion. An intermolecular contact 0.2 Å less than the sum of van der Waals radii exists between S2 and its equivalent related by inversion through the center of symmetry at $^1/_2$, $-^1/_2$, 0: S⋯S = 3.415 (1) Å.

c. Cd(II) Complex 10. This structure consists of polymeric chains of Cd(II) centers along the crystal *a* axis, linked by bis(μ-chloro) bridges and bridging thiadiazole macrocycle ligands; a portion of the chain is illustrated in Figure 4. There are two types of Cd centers, both with octahedral coordination, present in a 2:1 ratio. Cd1 lies on a center of symmetry and is coordinated by four bridging chloro ligands and two thiadiazole N atoms oriented trans. Bond distances are Cd1–Cl1 = 2.595 (1) Å, Cd1–Cl2 = 2.625 (1) Å, and Cd1–N2 = 2.495 (2) Å, and the angle subtended by the bis(μ-chloro) bridge is Cl1–Cd1–Cl2 = 89.97 (2)°. The second type of Cd(II) center lies in a general position and has less symmetric octahedral coordination. Two mutually cis sites are occupied by the bis(μ-chloro) bridge to Cd1, with distances Cd2–Cl1 = 2.633 (1) Å and Cd2–Cl2 = 2.555 (1) Å, subtending an angle Cl1–Cd2–Cl2 = 90.64 (2)°. The third site of the facial triple bridge is occupied by thiadiazole N, at a distance Cd2–N1 = 2.444 (2) Å. Two other coordination sites, trans to N1 and Cl2, are occupied by a centrosymmetric bis(μ-chloro) bridge to an adjacent Cd2′. This bridge, illustrated in Figure 5, is necessarily planar, with bond distances Cd2–Cl3 = 2.560 (1) Å and Cd2–Cl3′ = 2.607 (1) Å, subtending an angle Cl3–Cd2–Cl3′ = 89.51 (2)°. The sixth octahedral site is occupied by the oxygen atom of a methanol molecule, trans to the bridging chloro ligand Cl1, at a distance Cd2–O1M = 2.398 (2) Å. Intermetallic distances along the chain are Cd1⋯Cd2 = 3.5299 (2) Å and Cd2⋯Cd2′ = 3.6694 (3) Å. Cd–Cl–Cd angles at bridging chloro ligands are 84.94 (2)° at Cl1, 85.90 (2)° at Cl2, and 90.49 (2)° at Cl3.

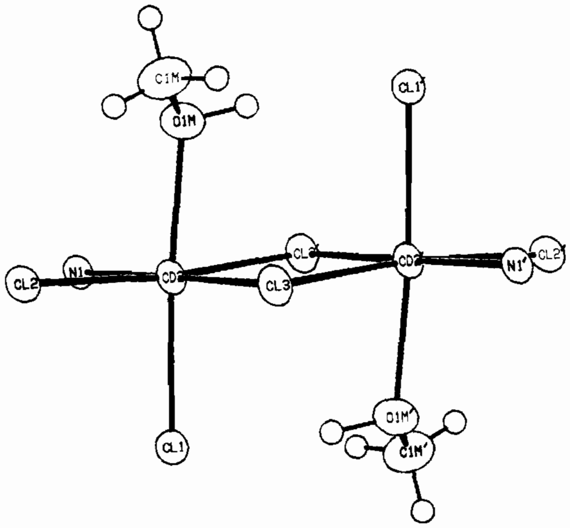

Figure 5. Centrosymmetric bis(μ-chloro) bridge of the Cd(II) complex **10**. The inversion center relates unprimed to primed atoms. Ellipsoids are drawn at the 50% probability level.

Incorporation as a bridging ligand into a triply bridging system imparts no significant structural changes in the thiadiazole macrocycle, save for conformational changes in the flexible polyether chain. The five-membered heterocyclic ring is planar, with a maximum deviation from the best plane of 0.005 (2) Å. Coordinated metal centers lie slightly (Cd2, 0.068 (1) Å) and appreciably (Cd1, −0.281 (1) Å) out of this plane. Geometrical parameters within the thiadiazole ring exhibit excellent agreement with those in the uncomplexed macrocycle and in the Cu(II) complex: N1–N2 = 1.374 (2) Å, C–N(av) = 1.306 (2) Å, C–S(av, endocyclic) = 1.721 (2) Å, C–S (av, exocyclic) = 1.744 (7) Å, C1–S1–C2 = 87.4 (1)°. Torsion angles describing the linkage of the polyether chain to the heterocycle are S1–C1–S2–C3 = −74.3 (2)° and S1–C2–S3–C10 = −11.3 (2)°, being respectively larger and smaller than those found in the other two compounds. The overall conformation of the macrocyclic ligand is similar to that seen in the Cu complex **9**. The thermal parameters of the C and O atoms are likewise small, with values ranging 1.8–3.5 Å^2. A similar but shorter intermolecular contact resembles that seen in the Cu complex. In this case, S2 forms a contact of 3.357 (1) Å with its equivalent by inversion through $^1/_2$, $^1/_2$, 0.

Electronic and EPR Spectra. The electronic and EPR spectral data of complexes **6**–**9** are listed in Table VII. The electronic spectra of Cu(II), Co(II), and Ni(II) nitrate complexes **6**–**8** in acetonitrile solution are typical of octahedral species, thus suggesting that solvent molecules are coordinated to the central metal ion. The spectral bands shown by the Co(II) complex **7** have been assigned to the following transitions: ν_1 = 8100 cm^{-1}, $^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$; ν_2 = 19 300 cm^{-1}, $^4A_{2g}(F) \leftarrow {}^4T_{1g}(F)$; ν_3 = 21 200 cm^{-1}, $^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$. These can be fitted by *10Dq* = *11 200* cm^{-1} and *B* = 1080 cm^{-1}.[15] As for the Ni(II) complex **8**, the following attributions have been made: ν_1 = 9300 cm^{-1}, $^3T_{2g} \leftarrow {}^3A_{2g}$; ν_2

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(15) Figgis, B. N. *Introduction to Ligand Field Theory*; Interscience: New York, 1966.

$= 17\,700$ cm^{-1}, $^3T_{1g}(F) \leftarrow {}^3A_{2g}$; $\nu_3 = 25\,700$ cm^{-1}, $^3T_{1g}(P) \leftarrow {}^3A_{2g}$. These yield $10Dq = 9300$ cm^{-1} and $B = 900$ cm^{-1}.

The spectral data associated with the Cu(II) complexes deserve a brief comment. The EPR spectrum of the Cu(II) nitrate complex **6** in acetonitrile (Table VII) is suggestive of an octahedral environment around the copper ion, consistent with the stereochemistry proposed for the analogous Co(II) and Ni(II) nitrate complexes **7** and **8**. When the Cu(II) bromide complex **9** is considered, the band richness of its electronic spectrum and the shifts of the spin Hamiltonian parameters (lower $g_\parallel$ and higher $A_\parallel$ values) suggest that the square-planar stereochemistry found in the solid state is also retained in acetonitrile or chloroform solution.

Concluding Remarks. 4,7,10-Trioxa-1,13-dithia[13](2,5)-1,3,4-thiadiazolophane (**5**) gives discrete 2:1 (ligand to metal) complexes with Cu(II), Co(II), and Ni(II) ions, and the solid-state structure of the complex with $CuBr_2$ has shown that the ligand does not accommodate the metal ion inside the cavity but rather coordinates on the exterior through the ring nitrogen atom. Although the hole size of the macrocycle is large enough to include a metal ion, complexation of transition metals inside the cavity is apparently disfavored by the poor coordinating ability of the hard polyether chain and by the lack of cooperativeness from exo- and/or endocyclic sulfur atoms, whose donor properties are greatly reduced by the resonance interaction of their unshared electron pairs with the π electrons of the heterocyclic ring.

Studies in solution of complexes of **5** with Cu(II), Co(II), and Ni(II) nitrates have suggested the formation of an octahedral environment around the central metal ion. However, experimental evidence is not conclusive for establishing the occupancy of the other coordination sites by nitrate groups and/or solvent molecules. In other words, not only is the nitrate group unlikely to act as a bidentate ligand but it is also plausible that it lies out of the coordination sphere.

Cu(II), Co(II), and Ni(II) complexes **6**–**8** failed to give crystals suitable for an X-ray structural investigation; therefore, a comparison of the stereochemistry in the solid state and solution could not be done, even though we need to say that a possible interaction of the nitrate groups with the free coordination positions of the complexed metal ion cannot be ruled out in the solid state.

In the case of the $CuBr_2$ complex **9**, both visible and EPR spectra have provided evidence of a direct participation of bromide ligands in the coordination sphere; thus, the solid-state square-planar coordination around the copper cation is retained in solution.

The reaction of **5** with anhydrous $CdCl_2$ in methanol afforded the polynuclear complex **10**, having two different octahedrally coordinated metal centers. Cadmium halides are known to form polymeric compounds, and there is evidence for polymerization of $CdCl_2$ in aqueous solution, also.[16] Therefore, the formation of a polynuclear structure of composition $[L_2(CdCl_2)_3{\cdot}2MeOH]_n$ is not unexpected, if one takes into account the probable preexistence of polymeric $CdCl_2$ in methanol solution, which may gain further stability by complexation with the bridging macrocyclic thiadiazole ligands.

Future research work in this field will be directed toward the synthesis of modified thiadiazole-containing macrocycles that eventually permit complexation of transition metals inside the cavity as well as macrocylic hole-size discrimination, our ultimate goal being their potential use as analytical reagents and catalysts.

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Registry No. **5**, 6663-97-4; **6**, 123810-08-2; **7**, 123775-13-3; **8**, 123775-14-4; **9**, 123753-21-9; **10**, 123753-22-0.

Supplementary Material Available: A complete listing of crystal data and data collection parameters, Tables SI–SV, SVII–SXIII, and SXV–SXIX, listing coordinates for hydrogen atoms, bond distances and angles, bond distances and angles involving H atoms, torsion angles, and anisotropic thermal parameters for **5**, **9**, and **10**, respectively, and Figures SI–SIII, giving stereoscopic plots of the packing for the three crystal structures (23 pages); Tables SVI, SXIV, and SXX, listing observed and calculated structure factors for **5**, **9**, and **10**, respectively (45 pages). Ordering information is given on any current masthead page.

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(16) Macklin, J. W.; Plane, R. A. *Inorg. Chem.* **1970**, *9*, 821 and references therein.