(4 H, 2 s, Mes–H), 7.02 (3 H, m, Ph–H). C_6D_6: δ 2.07, 2.21 (6 H, 2 s, *p*-Me), 2.40 (6 H, s, *o*-Me), 2.42 (6 H, s, *o*-Me), 6.70 (2 H, s, Mes–H), 6.80 (3 H, m, Ph–H), 6.89 (2 H, s, Mes–H), 7.06 (2 H, s, Ph-H). Anal. Calcd for $C_{26}H_{27}Cl$: C, 83.29; H, 7.26. Found: C, 83.03; H, 7.41.

Solvolysis–Cyclization of Trimesitylvinyl Chloride in Alcohols. In an aluminum foil covered ampoule a mixture of trimesitylvinyl chloride (50 mg, 1.25 mmol) and $AgBF_4$ (50 mg, 0.25 mmol) in ROH (R = Me, Et, *i*-Pr, *t*-Bu) (10 mL) was dissolved by heating, and the ampoule was kept at 80 °C for 48 h. The mixture was then poured into water (20 mL) and extracted with $CHCl_3$ (2 × 10 mL), and the organic phase was dried and evaporated. The residue was dissolved in $CDCl_3$ and the **5**/**7** ratio was determined by the relative integration of the indene-CH_2 signal to the methyl group(s) of the alkyl residue of **7**.

In addition, the reaction in *i*-PrOH was conducted on a larger scale: **5** (200 mg, 0.5 mmol) and $AgBF_4$ (200 mg, 1 mmol) in *i*-PrOH (20 mL) were heated in the dark to 110 °C for 24 h. After workup as above, 180 mg of a 85:15 **5**:**7**, R = *i*-Pr (by NMR) was obtained. On a silica TLC plate the R_f's with petroleum ether were 0.3 (**5**) and 0.11 (**7**).

Chromatography on a preparative TLC plate gave **5** (81 mg, 42%), mp 185 °C, and isopropyl trimesitylvinyl ether (17 mg, 8%), mp 167 °C, which was identical with the sample prepared previously by the phase transfer catalysis alkylation of **2**.[5b]

When the reaction of **6** (25 mg, 0.06 mmol) in *t*-BuOH (10 mL) was conducted in the absence of $AgBF_4$ for 96 h at 95 °C, the starting material was recovered unchanged.

Solvolysis of 8 in *tert*-Butyl Alcohol. To a solution of **8** (100 mg) in CCl_4 (0.5 mL) $AgBF_4$ (100 mg) and *t*-BuOH (10 mL) were added, and the mixture was heated in an ampoule in the dark at 95 °C for 48 h. The solvent was evaporated and the residue was dissolved in $CHCl_3$. The organic layer was washed with water, dried, and evaporated. ^1H NMR of the crude reaction mixture showed unreacted **8** and formation of several products. The main product was (*Z*)-1,2-dimesityl-2-phenylethenol[26], identified by ^1H NMR spectrum. The other minor compounds, including one which may be the *tert*-butyl ether (by NMR) were not investigated.

Acknowledgment. We are indebted to Prof. H. Schwarz and Prof. C. Lifshitz for the CI Mass Spectra of the isotopomeric indenes, to Dr. H.-U. Siehl for the reaction of **6** in superacid, to Dr. S. Cohen for the X-ray diffraction of **5**, to Dr. S. Kobayashi for the UV spectrum of **2**, and to Prof. H. Zollinger for discussions. This work was supported by a grant from the United States–Israel Binational Science Foundation (BSF), Jerusalem, Israel, to whom we are grateful.

Registry No. **2**, 26905-20-4; **5**, 100702-07-6; **5**-*1,1*-d_2, 100702-08-7; **6**, 87871-31-6; **7** (R = Et), 100702-09-8; **7** (R = *i*-Pr), 87871-30-5; **8**, 100702-10-1; T_4Cl, 98-59-9; D_2, 7782-39-0; (*Z*)-1,2-dimesityl-2-phenylethenol, 77787-79-2.

Supplementary Material Available: Tables S1–S3 giving the complete list of bond lengths, angles, and positional parameters for carbons of compound **5** and Figure 3 giving the stereoscopic view of **5** (4 pages). Ordering information is given on any current masthead page.

Polydentate Ketal Coronands Containing 2,6-Pyridino and/or 6,6′-(2,2′-Bipyridino) Subunits: Synthesis, Characterization, Structural Aspects, and Conformational Changes upon Complexation

George R. Newkome,* Hellen C. R. Taylor, Frank R. Fronczek, and Vinod K. Gupta

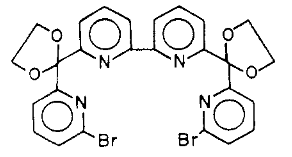
Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803-1804

Received August 7, 1985

Coronands were formed from 6,6′-bis[2″-(6‴-bromo-2‴-pyridyl)-1″,3″-dioxolan-2″-yl]-2,2′-bipyridine (1) and then hydrolyzed to the corresponding diketonic coronands. Comparative data from the X-ray crystal structures of the diketal coronand of bis(2-mercaptoethyl) ether and its Co(II) complex demonstrate that the same conformational preferences are embraced by the ketal assembly in both, but that the bipyridine moiety changes from anti in the coronand to syn in the complex. The Co(II) complex exhibited medium range interactions of *both* ketals *with* the metal and thus a bis-capped tetrahedral geometry.

Introduction

The immediate attachment of an oxygen or sulfur atom to the heteroaromatic ring of a pyridyl coronand subverts the ability of these compounds to engage in metal ion coordination.[1,2] Not only does the presence of an electron-withdrawing group in an α position on the pyridine ring vitiate the donor properties of the nitrogen[1,3] by virtue of the imidate (or thioimidate) function that results,[4] but approach to the N-lone pair is somewhat restricted sterically. The inclusion of a tetrahedral carbon atom between the pyridine and the first bridge heteroatom was envisioned as a solution: flexibility and basicity would be reinstated.[5] 6,6′-Bis[2″-(6‴-bromo-2‴-pyridyl)-1″,3″-dioxolan-2″-yl]-2,2′-bipyridine (**1**)[6] was utilized as the starting material for the construction of the macrocycles, as it contained 2,2′-bipyridine subunit which is a well-known chelating agent.[7] It has been noted in many 2,2-



1

---

(1) Schofield, K. "Heteroaromatic Nitrogen Compounds. Pyrroles and Pyridines"; Plenum Press: New York, 1967; p 145.

(2) Newkome, G. R.; Kawato, T. *J. Am. Chem. Soc.* **1979**, *101*, 7088. Newkome, G. R.; Majestic, V. K.; Fronczek, F. R. Atwood; J. L. *J. Am. Chem. Soc.* **1979**, *101*, 1047.

(3) Newkome, G. R.; Nayak, A.; Fronczek, F.; Kawato, T.; Taylor, H. C. R.; Meade, L.; Mattice, W. *J. Am. Chem. Soc.* **1979**, *101*, 4472.

(4) (a) Taskinen, E.; Mukkala, V.-M.; Pentikainen, M.-L. *Tetrahedron* **1979**, *35*, 547. (b) Vohra, S. K.; Harrington, G. W.; Zacharias, D. E.; Swern, D. *J. Org. Chem.* **1979**, *44*, 1128. (c) Lumbroso, H.; Palamidessi, G. *Bull. Soc. Chim. Fr.* **1965**, 3150.

(5) Newkome, G. R.; Majestic, V. K.; Fronczek, F. R. *Tetrahedron Lett.* **1981**, 3035.

(6) Fronczek, F. R.; Taylor, H. C. R.; Gupta, V. K.; Newkome, G. R. *Acta Cryst. C*, **1985** *C41*, 1548.

(7) McKenzie, E. D. *Coord. Chem. Rev.* **1971**, *6*, 187.

Table I. Physical and Spectral Data for Diketal Coronands

		^{1}H NMR[c]								IR,[h] cm^{-1}		
compd[a,b]	%	3-py H	4,5-py H	4′-py H[d]	3′-py H[e]	5′-py H[f]	ketal	α[g]	β[g]			MS
2a	68	8.22	7.70	7.63	7.43	6.64	4.22	4.06	2.76	1592	1460	556 (14)[i]
2b	65	8.16	7.76	7.65	7.48	6.67	4.25	4.14	3.23	1591	1457	600 (3)
2c	76	8.14	7.64	7.64	7.48	6.68	4.20		3.50	1597	1456	644 (2)
2d	17	8.14	7.74	7.63	7.47	6.68	4.17	4.24	3.55	1593	1455	668 (2)
2e	9	8.16	7.74	7.62	7.45	6.65	4.18	4.26	3.59	1589	1460	732 (3)
7	2	8.21	7.72, 7.58	7.33	7.12	6.61	4.21	3.65	3.25	1587	1458	194 (100)
5	75	8.20	7.70	7.55	7.55	7.16	4.21	2.50	2.43	1590	1456	558 (3)[j]

[a] Most coronands were oils, except for **2a** (mp 176–177 °C) and **5** (mp 230–230.5 °C). [b] All new compounds have satisfactory analytical data. [c] $CDCl_3$ solutions with Me_4Si, as the internal standard ($\delta = 0$ ppm). [d] $J = 8.2$, 7.3 Hz. [e] $J = 7.3$, 0.7 Hz. [f] $J = 8.2$, 0.7 Hz. [g] $J = 4.6 \pm 0.2$ Hz. [h] Neat samples, except for **5** (KBr). [i] m/e 166 (100). [j] m/e 136 (100).

Table II. Relative Yields of Glycol Fragmentation Products[a]

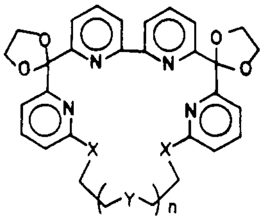
	relative percentages of macrocycle					
ethylene glycol	**2a**	**2b**	**2c**	**2d**	**2e**	total
di	68					68
tri	9	56				65
tetra	8	15	76			99
penta	3	5	9	17		34
hexa	1	2	4	9	9	25

[a] Yields based on **1**.

bis(2′-pyridyl)-1,3-dioxolane containing molecules that the pyridine rings are disposed with respect to the dioxolane ring in such a fashion that the nitrogen atoms are anti to oxygen.[6,8] In order to see if this is also true in complexes, the Co(II) chelate of the macrocycle **5** has been prepared and its single-crystal X-ray structure determined. A comparative evaluation of the conformational preferences of the free ligand to its cobalt complex will be conducted.

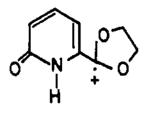
Results and Discussion

Treatment of **1** with the disodium salt of an oligoethylene glycol in toluene (90 °C) for several days afforded the desired diketal coronands (**2**). In the ^{1}H NMR spectra



2a, $n = 1$, X = Y = O
2b, $n = 2$, X = Y = O
2c, $n = 3$, X = Y = O
2c, $n = 3$, X = Y = O
2d, $n = 4$, X = Y = O
2e, $n = 5$, X = Y = O
5, $n = 1$, X = S, Y = O
7, $n = 1$, X = Y = S

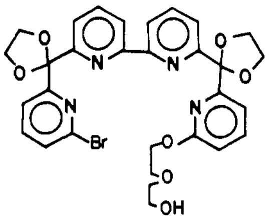
of **2a–e** (Table I) the peaks for the glycol protons[8] were quite similar and the ketal signal [which appears as a spike at an average value of δ 4.20 (± 0.03)] was a very complicated pattern. Except for the bipyridine H-4,5 signals which overlapped to give a multiplet, all the resonances were doublets of doublets and appeared at average chemical shift values: δ 6.66 (± 0.02), H-5′; 7.46 (± 0.03), H-3′; 7.63 (± 0.02), H-4′; 7.72 (± 0.04), H-4, 5; 8.16 (± 0.06), H-3. The downfield position of the H-3 signal indicated that, even in the smallest of the coronands, the bipyridine group was in the anti conformation.[9] The MS data of **2a–e** were quite conclusive[10,11] with regard to identification: the molecular ion was observed for each compound (Table I) and the base peak for each represented the pyridone ketal fragment **3**.



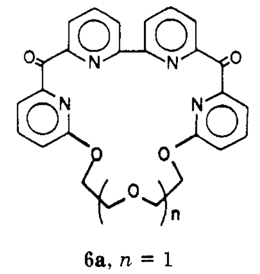
3

Reaction with diethylene glycol produced not only the desired coronand **2a** but an open-chained **4** as well. In sharp contrast,[8] this was the lone uncyclized compound isolated from any of the reactions herein discussed. The other glycols[12] gave products that arose from the parent compound and all smaller oligoethylene glycols,[13-15] except ethylene glycol itself. Thus, reaction of **1** with hexaethylene glycol afforded **2a–e**, in moderate yields. Table II lists the relative amounts of glycol fragmentation products. For reaction of **1** with tetraethylene glycol, virtually *all* of the substrate was converted to macrocycle. A reasonable explanation for this phenomenon is not apparent.

Unlike other diketals,[16,17] which were very difficult to hydrolyze, diketals **2** were smoothly converted to **6** upon refluxing in 1:1 MeOH/6 M HCl for 3 days (Table III).



4



6a, $n = 1$
6b, $n = 2$
6c, $n = 3$
6d, $n = 4$
6e, $n = 5$

---

(8) Newkome, G. R.; Taylor, H. C. R.; Fronczek, F. R.; Delord, T. J. *J. Org. Chem.* **1984**, *49*, 2961.

(9) (a) McInnes, A. G.; Smith, D. G.; Walter, J. A.; Wright, J. L. C.; Arseneault, G. P. *Can. J. Chem.* *1978*, *56*, 1836. (b) McInnes, A. G.; Smith, D. G.; Wright, J. L. C.; Vining, L. C. *Ibid.* **1977**, *55*, 4159. (c) Calder, I. C.; Spotswood, T. M.; Tanzer, C. I. *Aust. J. Chem.* **1967**, *20*, 1195. (d) Castellano, S.; Günther, H.; Ebersole, S. *J. Phys. Chem.* **1965**, *69*, 4166. (e) Kramer, F. A., Jr.; West, R. *Ibid.* **1965**, *69*, 673.

(10) Barnes, C. S.; Groldsack, R. J.; Halbert, E. J.; Wilson, J. G.; Lyall, R. J.; Middleton, S. *Tetrahedron Lett.* **1972**, 705.

(11) Keats, N. G.; Summers, L. A. *J. Heterocycl. Chem.* **1976**, *13*, 1289.

(12) Professor K. Potts (Rensselaer Polytechnic Institute), personal communication, 1980.

(13) Staude, E.; Patai, F. In "The Chemistry of the Ether Linkage"; Patai, S., Ed.; Interscience: New York, 1967; p 46.

(14) Lubowicz, R. E.; Reich, P. *Chem. Eng. Prog.* **1971**, *67*, 59.

(15) Mattice, W.; Newkome, G. R. *J. Am. Chem. Soc.* **1979**, *101*, 4477.

(16) Newkome, G. R.; Nayak, A.; Sauer, J. D.; Mattschei, P. K.; Watkins, S. F.; Fronczek, F. R.; Benton, W. H. *J. Org. Chem.* **1979**, *44*, 3816.

(17) Fronczek, F. R.; Watkins, S. F.; Newkome, G. R. *J. Chem. Soc., Perkin Trans. 2* **1981**, 877.

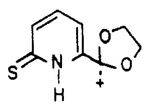
Table III. Physical and Spectral Data for Diketonic Coronands

		^{1}H NMR												
compd[a]	%	3-py H[b]	4-py H[c]	3′-py H[d]	4′-py H[d]	5-py H[d]	5′-py H	α[e]	β	$\gamma(\delta-\epsilon)$	IR,[f] cm^{-1}			MS, M$^+$
6a	71	8.28	7.90		7.70	7.72	6.93	4.09	3.24		1682	1590	1460	468 (60)
6b	99	8.57	7.94	7.80	7.80	7.80	6.98	4.28	3.59	3.38	1678	1583	1454	512 (63)
6c	86	8.58	7.95	7.95	7.81	7.81	7.01	4.29	3.71	3.55	1678	1600	1457	556 (56)
6d	87	8.59	7.98	7.95	7.81	7.81	7.02	4.34	3.70	3.52	1681	1592	1459	600 (15)
6e	81	8.59	7.98	7.98	7.91	7.91	7.02	4.34	3.70	3.52	1677	1592	1454	644 (18)

[a] All compounds were oils. [b] J = 7.9, 1.1 Hz. [c] J = 7.9, 7.9 Hz. [d] Multiplets. [e] J = 4.7–5.6 Hz. [f] Spectra were obtained from neat samples.

Progress of the reaction was monitored by TLC (silica): the diketones produced the characteristic green-brown color at 366 nm. Deprotection of the ketones was verified by the appearance of a carbonyl stretching band at ca. 1680 cm^{-1} in the IR spectra of **6**, and by the downfield shifts ($\Delta\delta \cong 0.3$) of pyridine H-5′ in the ^{1}H NMR spectra. The general diamagnetic shift reflects the increased electron-withdrawing character of the pyridyl ketone group with respect to a pyridyl ketal. This effect is a consequence of the delocalization of π-electron density from the pyridines onto the carbonyl oxygen. The relative simplicity of these spectra (Table III) indicated symmetry in the molecule. Furthermore, the MS data for each ketone displayed a molecular ion.

Subjection of **1** to the disodium salt of bis(2-mercaptoethyl) sulfide in toluene afforded (2%)[18] coronand **7**, as a yellow oil. The ^{1}H NMR spectrum of **7** (Table I) bears a strong resemblance to but is not identical with that of **2b**. Replacement of the bridge oxygens by less electronegative sulfur[19-21] shifts the α-methylene signals upfield (δ 3.65), as well as for the H-3′ and H-4′ signals (δ 7.12 and 7.33, respectively). There is no parent peak evident in the MS data (Table I), but the base peak corresponds to the thiopyridone ketal fragment (m/e 194) **8**.



8

When **1** was treated with the disodium salt of bis(2-mercaptoethyl) ether under the same conditions described for the glycols, the product **5** was obtained (75%) as a colorless oil, that crystallized by slow evaporation of an EtOH/CH$_3$CN solution. Again, the ^{1}H NMR data (Table I) reflected the change of the first bridge heteroatom from oxygen to sulfur: for **5**, only the resonances of the α-methylene hydrogens and H-5′ were significantly different from the oxygen analogues. The peaks for the α-protons were shifted to α 2.50, even farther upfield than for **7**. The resonance for H-5′ occurred at δ 7.16, far downfield ($\Delta\delta$ = 0.5) of the corresponding signal of **2** or **7**. Although the mass spectrum (Table I) showed a molecular ion at m/e 558 which corresponded to the molecular ion of **5**, the disparity in the ^{1}H NMR spectra of **7** and **5** occasioned an X-ray structure analysis of the latter.

The ORTEP drawing of **5** is illustrated in Figure 1 and the selected bond distances and angles are presented in Table IV. The most striking feature of its solid state conformation was the anti disposition of the central bipyridino group: the N1–C1–C26–N4 torsion angle is 175.7°. The pyridines are planar and turned with respect to the dioxolane rings such *that the nitrogens are essentially anti to the oxygen*. Thus, N1–C5–C6–O2 is 172.0°, N2–C7–C6–O3 is 171.1°, and the dihedral angle between the nonconjugated pyridines is 104.4°. Torsion angles about the other dioxolane are 169.0° for N4–C22–C21–O5 and 173.6° for N3–C20–C21–O4; the dihedral angle between these pyridines is 104.2°. The dioxolane rings are nonplanar. The torsion angles of the thioimidate linkage are larger than those generally observed when oxygen is adjacent to the heteroaromatic ring: −17.1° and −6.3° for N2–C11–S1–C12 and N3–C16–S2–C15, respectively. The thioether bridge consists of only seven atoms, but is of sufficient length to prevent real strain or distortion in the

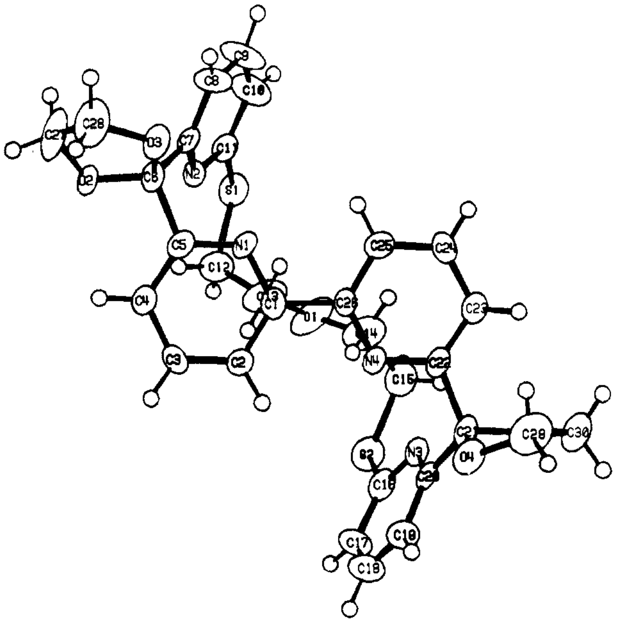


Figure 1. ORTEP of **5**.

Table IV. Selected Bond Distances (Å) and Angles (deg) for 5 and 9

	distance			angle	
atoms	**5**	**9**	atoms	**5**	**9**
S1–C11	1.778 (3)	1.754 (6)	C11–S1–C12	102.0 (2)	105.1 (3)
S2–C16	1.769 (4)	1.780 (6)	C15–S2–C16	102.3 (2)	101.0 (3)
N1–C1	1.342 (4)	1.352 (5)	C13–O1–C14	111.0 (3)	113.2 (4)
N1–C5	1.339 (4)	1.339 (6)	C1–N1–C5	116.8 (3)	119.7 (4)
N2–C7	1.352 (4)	1.352 (6)	C7–N2–C11	117.8 (3)	116.5 (4)
N2–C11	1.331 (4)	1.337 (6)	C16–N3–C20	117.5 (3)	117.2 (5)
N3–C16	1.334 (4)	1.352 (6)	C22–N4–C26	117.9 (3)	119.0 (4)
N3–C20	1.348 (4)	1.323 (6)	C5–C6–C7	109.9 (3)	111.8 (4)
N4–C22	1.339 (4)	1.346 (6)	O2–C6–O3	107.4 (3)	107.7 (4)
N4–C26	1.333 (4)	1.367 (6)	C20–C21–C22	111.2 (3)	110.5 (4)
C1–C26	1.505 (5)	1.472 (7)	O4–C21–O5	106.1 (3)	106.1 (4)
Co–Cl1		2.273 (1)	Cl1–Co–Cl2		137.61 (6)
Co–Cl2		2.251 (1)	Cl1–Co–N1		103.61 (11)
Co–N1		2.072 (4)	Cl1–Co–N4		102.04 (11)
Co–N4		2.136 (4)	Cl2–Co–N1		113.12 (11)
			Cl2–Co–N4		104.84 (11)
			N1–Co–N4		79.25 (15)

---

[18] Mattice, W. *J. Am. Chem. Soc.* **1980**, *102*, 2242.

[19] Abramovitch, R. A.; Newman, A. J. *J. Org. Chem.* **1974**, *39*, 2690.

[20] Ochrymowycz, L. A.; Mak, C.-P.; Michna, J. D. *J. Org. Chem.* **1974**, *39*, 2079.

[21] Black, D. St. C.; McLean, I. A. *Tetrahedron Lett.* **1969**, 3961.

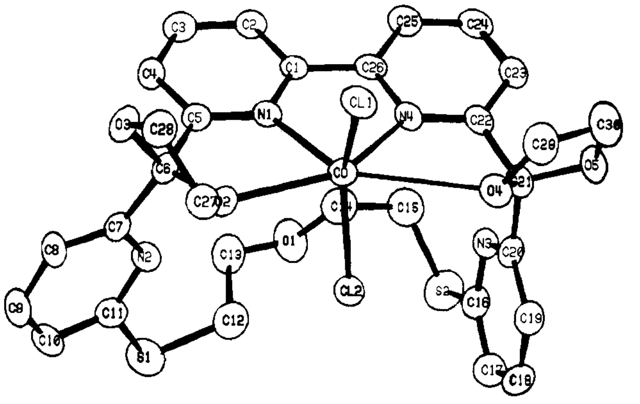


Figure 2. ORTEP of 9.

rest of the molecule, which has very nearly C_2 symmetry.

Reaction of 5 with $CoCl_2{\cdot}6H_2O$ produced a brightly colored complex 9, which decomposed above 250° and displayed a 1:1 metal to ligand stoichiometry, as indicated by the elemental analysis. Slow evaporation of the methanolic solution gave crystals of 9 suitable for X-ray diffraction studies.

Dark turquoise prisms of 9 were found to consist of neutral molecules containing Co(II) N-chelated by the bipyridino moiety (N1 and N4) and two chloro ligands. As illustrated in Figure 2, the metal is *also* involved in interactions with O2 and O4 of the dioxolane rings. The Co–O distances are different [2.404 (3) Å and 2.868 (3) Å for Co-O2 and Co-O4, respectively], but both are similar to the values observed for monoketals.[22] Selected bond distances and angles for 9 are compiled in Table IV. Partial coordination by the nonplanar dioxolane rings and a dihedral angle near 90° between the N1–Co–N4 and Cl1–Co–Cl2 planes (Figure 2) indicates a geometry about the metal that is best described as a *bis*-capped tetrahedron. The Co–O2 vector essentially bisects the N1–Cl1–Cl2 face, as the Co–O4 does the N4–Cl1–Cl2 face. The constraints of the dipyridine moiety distort the tetrahedron to some extent: the "bite" angle of the nitrogens is 79.25 (15)°, whereas the angle between the larger chloro ligands is 137.61 (6)°. Probably as a result of the α-S-substitution at the 6-position of the pyridines, N2 and N3 do not act as donors to the cobalt(II); this further substantiates the diminished donor properties of pyridines possessing a (thio)imidate group.

The disposition of the pyridines with respect to the dioxolane rings is such that the nitrogens are anti to oxygen. In order to accommodate Co chelation, however, the usual pyridyl ketal geometry is distorted somewhat. The torsion angle for N2–C7–C6–O3 is 164.6°, but that of N1–C5–C6–O3 is only 119.8°. The deformation is similar for the other dioxolane: the torsion angle for N4–C22–C21–O5 is −160.0°, whereas that for N3–C20–C21–O4 is 137.6°. The torsion angles of the thioimidate linkages match those of the uncomplexed ligand: 7.5° for N2–C11–S1–C12 and −21.7° for N3–C16–S2–C15.

Conclusion

The incorporation of a tetrahedral carbon atom between the pyridine and the first bridge heteroatom results in ligand systems with better complexation properties. The macrocycle 5 and its Co(II) complex 9 exhibited the same conformational preferences for the ketal functionality except for the pyridine moiety which changes from anti in the coronand to syn in the complex.

Table V. Crystal Data and Data Collection Parameters

	5	9
formula	$C_{30}H_{28}N_4O_5S_2$	$C_{30}H_{28}N_4O_5S_2{\cdot}CoCl_2$
FW	588.7	718.6
crystal system	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a, Å	13.480 (2)	10.875 (4)
b, Å	13.854 (4)	11.504 (4)
c, Å	16.387 (6)	13.384 (6)
α, deg		81.50 (3)
β, deg	106.77 (3)	81.98 (3)
γ, deg		66.06 (3)
V, Å^3	2930 (3)	1507.7 (10)
Z	4	2
D_{calcd}, g cm^{-3}	1.334	1.583
μ (Mo Kα), cm^{-1}	2.2	9.3
2θ limits, deg	2–45	2–44
precision	$I = 25\sigma(I)$	$I = 25\sigma(I)$
scan speeds, deg min^{-1}	0.45–20.0	0.59–5.0
crystal size, mm	0.30 × 0.32 × 0.40	0.15 × 0.26 × 0.36
min. rel. trans. coeff., %		80.06
unique data	3821	3673
observed data	2136	2516
refined variables	370	397
R	0.046	0.039
R_w	0.057	0.043
residual density, e Å^{-3}	0.36	0.33
T, °C	24	23

Experimental Section

General Comments. Melting point data were obtained in capillary tubes with a Thomas-Hoover Unimelt apparatus and are uncorrected. IR spectra were measured on a Perkin-Elmer 621 Grating Spectrophotometer. NMR spectra were measured on a Bruker WP-200 Spectrometer in $CDCl_3$ solution with Me_4Si, as an internal standard (δ = 0 ppm). MS data were obtained at 70 eV by D. A. Patterson on a Hewlett-Packard Model 5985 GC/MS Spectrometer and reported herein as (assignment, relative intensity). Preparative thick-layer chromatography (ThLC) was performed on 20 × 40 cm glass plates coated with a 2-mm layer of Brinkmann Silica Gel P/UV-254-366. Elemental analyses were performed in these laboratories by R. L. Seab.

Toluene and xylene were distilled from sodium wire under an inert atmosphere. The NaH (57% oil dispersion) was washed with anhydrous petroleum ether (bp 30–60 °C) and dried in vacuo prior to the reaction. Ethylene glycol and di-, tri-, and tetraethylene glycols were purchased from Aldrich Chemical Company. The penta- and hexaethylene glycols[23] were acquired from Columbia Organic Chemicals, Inc.

Reaction of 6,6′-Bis[2″-(6‴-bromo-2‴-pyridyl)-1″,3″-dioxolan-2″-yl]-2,2′-bipyridine with Poly(ethylene glycols). A General Coronand Preparation. A suspension of oil-free NaH (120 mg, 5 mmol) in anhydrous toluene (100 mL) was stirred under a N_2 atmosphere for 10 min. Addition of the glycol or thiol (0.5 mmol) in anhydrous toluene (25 mL) resulted in the formation of a viscous grey mass and copious H_2 evolution. After 30 min, all effervescence had ceased and solid 1 (306 mg, 0.5 mmol) was added, followed by toluene (25 mL). The mixture was stirred at 90 °C for 5 days, *carefully* quenched with H_2O, and concentrated in vacuo. The aqueous slurry was extracted with CH_2Cl_2 (4 × 75 mL), and the combined organic extract was dried over anhydrous $MgSO_4$ and evaporated in vacuo. Further purification was achieved by thick layer chromatography. Table I summarizes the pertinent physical and spectral data.

Hydrolysis of Diketal Coronands 2. A General Procedure. A solution of 2 (0.4 mmol), aqueous HCl (10 mL, 6 M), and MeOH (10 mL) was refluxed for 72 h. After the MeOH was removed in vacuo, the acidic residue was neutralized with 10% Na_2CO_3 and extracted with $CHCl_3$ (4 × 50 mL). The combined organic

---

[22] Newkome, G. R.; Taylor, H. C. R.; Fronczek, F. R.; Gupta, V. K. *Inorg. Chem.*, in press.

[23] Reddy, C. P.; Rao, R. B. *Tetrahedron* **1982**, *38*, 1825.

extract was dried and concentrated to afford the diketone coronands **6**. Further purification was achieved by thick layer chromatography. Table III summarizes the physical and spectral data.

Complexation of 5 with Cobalt(II) Chloride. A solution of **5** (58.8 mg, 0.1 mmol) in $CHCl_3$ was added to a solution of $CoCl_2 \cdot 6H_2O$ (0.1 mmol) in MeOH (5 mL). After 4 h at reflux, the mixture was concentrated in vacuo to a volume of 5 mL, and the remaining solvent was allowed to evaporate slowly.

X-ray Experimental Methods. Intensity data for **5** and **9** were collected on an Enraf-Nonius CAD4 diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. Variable scan rates were employed in the ω–2θ scans in order to achieve approximately equal relative precision for all observable data. One quadrant of data was collected for the monoclinic crystal; one hemisphere for the triclinic crystal. Crystal data and angular limits for each compound are given in Table V. Data reduction included corrections for background, Lorentz, and polarization effects. Absorption corrections for the complex were based on ψ scans of reflections near χ = 90°. Equivalent data were averaged and reflections having $I > 3\sigma(I)$ were used in the refinements.

Structures were solved using MULTAN 78[24] and refined by full-matrix least squares based on F with weights $w = \sigma^{-2}(Fo)$. Non-hydrogen atoms were treated anisotropically; H atoms were located by difference maps and included as fixed contributions. Final R factors and residual electron densities are given in Table V.

Acknowledgment. We wish to thank the National Science Foundation, the National Institutes of Health, and LSU Center for Energy Studies for partial support of this work.

Supplementary Material Available: Coordinates for non-hydrogen atoms for **5** and **9**, bond distances and angles for **5** and **9**, coordinates for hydrogen atoms for **5** and **9**, anisotroic thermal parameters for **5** and **9**, and stereoscopic drawing of **5** (11 pages). Ordering information is given on any current masthead page.

---

[24] Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M., "MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data"; Universities of York (England) and Louvain (Belgium), 1978.

[2 + 2] and [2 + 4] Cycloadditions of Difluoromethylenecyclopropanes

William R. Dolbier, Jr.,* Mark Seabury, and Daniel Daly

Department of Chemistry, University of Florida, Gainesville, Florida 32611

Bruce E. Smart*[1]

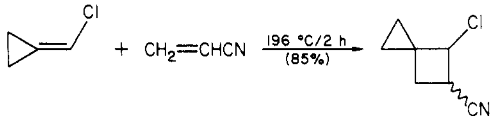
Central Research & Development Department, Experimental Station, E. I. du Pont de Nemours & Co., Wilmington, Delaware 19898

Received September 10, 1985

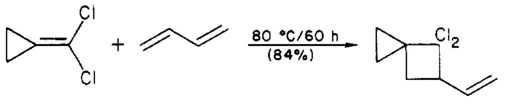
An improved synthesis of 2,2-difluoromethylenecyclopropane (**1**) is reported and its thermal cycloaddition reactions are compared with those of its isomer, (difluoromethylene)cyclopropane (**2**). 2,2-Difluoromethylenecyclopropane readily reacts with dienes in a [2 + 4] manner, whereas **2** predominantly undergoes [2 + 2] cycloadditions, including cyclodimerization. The factors that influence the reactivities of **1** and **2** are discussed.

Methylenecyclopropanes are relatively unreactive addends in cycloadditions. Some undergo thermal [2 + 2] dimerizations forming cyclobutanes,[2] as exemplified by methylenecyclopropane itself which will cyclodimerize in a head-to-head manner, but only to the extent of about 20% in 48 h at 245 °C.[2b] Certain radical-stabilizing substituents greatly enhance reactivity. (Dichloromethylene)cyclopropane, for instance, readily cyclodimerizes in high yield at 100 °C.[2d] The dimerizations, however, are quite sensitive to steric effects, inasmuch as that ethylidenecyclopropane,[3] isopropylidenecyclopropane,[2a] and 2,2-dimethylmethylenecyclopropane[2a] do not thermally cyclodimerize.

Methylenecyclopropanes also have been reported to undergo other [2 + 2] cycloadditions as shown in eq 1 and 2, although the examples are few.[2c,4]



(1)



(2)

The [2 + 2] cycloaddition reactions of methylenecyclopropanes are presumed to proceed via a two-step, biradical mechanism wherein the first step involves σ-bond formation to the highly strained sp^2-hybridized carbon of the methylenecyclopropane to give the most stable biradical intermediate, which determines the favored regiochemistry.[5] This mechanism is exemplified in eq 3 for the reaction of (dichloromethylene)cyclopropane with butadi-

---

[1] Contribution No. 3866.

[2] (a) Dolbier, W. R., Jr.; Lomas, D.; Garza, T.; Harmon, C.; Tarrant, P. *Tetrahedron* **1972**, *28*, 3185. (b) Binger, P. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 433. (c) Bottini, A. T.; Cabral, L. J. *Tetrahedron* **1978**, *34*, 3187. (d) Dolbier, W. R., Jr.; Lomas, D.; Tarrant, P. *J. Am. Chem. Soc.* **1968**, *90*, 3594. (e) Le Perchec, P.; Conia, J. M. *Tetrahedron Lett.* **1970**, 1587.

[3] Chesick, J. P. *J. Am. Chem. Soc.* **1963**, *85*, 2720.

[4] Bartlett, P. D.; Wheland, R. C. *J. Am. Chem. Soc.* **1972**, *94*, 2145.

[5] An exceptional case is the reported [2 + 2] cycloaddition of 4-phenyl-1,2,4-triazoline-3,5-dione to *trans*-2,3-dimethylmethylenecyclopropane[6a] for which a biradical mechanism is unlikely.[6b,c]

[6] (a) Pasto, D. J.; Chen, A. F. T. *Tetrahedron Lett.* **1972**, 2995. (b) Seymour, C. A.; Greene, F. D. *J. Am. Chem. Soc.* **1980**, *102*, 6385. (c) Cheng, C.-C.; Seymour, C. A.; Petti, M. A.; Greene, F. D.; Blount, J. F. *J. Org. Chem.* **1984**, *49*, 2910.

0022-3263/86/1951-0974$01.50/0