ment of new molecular magnetic materials with interesting properties or combination of properties. Attempts are in progress.

Acknowledgment. This work was supported by the Comisión Interministerial de Ciencia y Tecnologia (Grant MAT89-177), by the Spanish-French Integrated Action TM-189, and by the Institució Valenciana d'Estudis i Investigació. We are deeply grateful to the Centre de Recherches Paul Pascal (Talence, France) for allowing us the use of the SQUID magnetometer and to C. Zanchini from the Dept di Chimica of Florence for her help in the low-temperature EPR measurements. It is a pleasure to acknowledge enthusiastic discussions with Prof. L. C. W. Baker in the exciting area of polyoxoanions. C.J.G.-G. and J.J.B.-A. thanks the Ministerio de Educación y Ciencia for a grant. E.C. thanks the Generalitat Valenciana for a travel grant.

Registry No. I, 98773-81-0; II, 97836-72-1; III, 98743-06-7; IV, 97836-71-0.

Contribution from the Departments of Chemistry, University of California, San Diego, La Jolla, California 92093-0314,
and University of Missouri, Columbia, Missouri 65211

Synthesis and Structures of the Bis(*cis*-1-methylthiostilbene-2-thiolate) of Cadmium and Its Adducts with Dimethyl Sulfoxide, 4-(Dimethylamino)pyridine, and 2,2'-Bipyridyl: Hexacoordination of Cadmium vs Pentacoordination in the Corresponding Zinc Derivatives

Hussain K. Reddy,[†] Cheng Zhang,[‡] E. O. Schlemper,[*,§] and G. N. Schrauzer[*,‖]

Received August 19, 1991

Whereas the zinc derivative of *cis*-1-methylthiostilbene-2-thiol forms a well-defined μ-S-bridged dimer of composition $Zn_2[Ph(SCH_3)C{=}C(S)Ph]_4$ with pentacoordinated zinc, the corresponding compound of cadmium appears to have a polymeric structure. However, it forms a well-defined μ-S-bridged dimeric 1:1 adduct with dimethyl sulfoxide (DMSO), $Cd[Ph(SCH_3)C{=}C(S)Ph]_2(DMSO)$, of composition $C_{32}H_{32}S_5CdO$, with hexacoordinated cadmium, crystallizing in the triclinic space group $P\bar{1}$ with unit cell parameters $a = 11.529$ (4) Å, $b = 12.955$ (5) Å, $c = 22.804$ (8) Å, $\alpha = 106.480$ (20)°, $\beta = 92.590$ (20)°, and $\gamma = 94.680$ (20)°, with $Z = 2$. The coordination geometry of the cadmium ions is distorted octahedral, the DMSO is coordinated via oxygen, and the Cd–O bond length is 2.358 (6) Å. The sulfur ligands are bound in an anisobidentate fashion, with normal covalent Cd–S and Cd–μ-S bonds of 2.5072 (22) and 2.6364 (22) Å and elongated coordinative Cd–S bonds of 2.8045 (22) and 2.976 (3) Å, respectively. On reaction with 4-(dimethylamino)pyridine (dmapy), a hexacoordinated 1:2 adduct, $Cd[Ph(CH_3S)C{=}C(S)Ph]_2(dmapy)_2$, of composition $C_{44}H_{46}N_2S_4Cd$ is formed, which crystallizes in the monoclinic space group $C2/c$ with $a = 17.483$ (4) Å, $b = 12.290$ (3) Å, $c = 19.963$ (5) Å, $\beta = 98.998$ (20)°, and $Z = 4$. The mean covalent Cd–S and coordinate Cd–N bond distances of 2.556 (1) Å and 2.384 (4) Å are within normal ranges, and the mean coordinate Cd–S bonds of 2.869 (2) Å are elongated but genuine coordinate bonds. The coordination geometry of Cd is distorted octahedral, and the dmapy molecules are in cis positions opposing the coordinate Cd–S bonds. The adduct with 2,2'-bipyridyl (bpy), $Cd[Ph(SCH_3)C{=}C(S)Ph]_2(bpy)$, of composition $C_{40}H_{34}N_2S_4Cd$, also contains hexacoordinated Cd and crystallizes in the triclinic space group $P\bar{1}$, with $a = 13.652$ (3) Å, $b = 12.843$ (7) Å, $c = 10.5640$ (20) Å, $\alpha = 101.39$ (3)°, $\beta = 94.200$ (20)°, $\gamma = 94.36$ (3)°, and $Z = 2$. The mean covalent and mean coordinate Cd–N bond lengths of 2.5260 (13) and 2.382 (36) Å are normal; the coordinate Cd–S bonds of 2.8151 (19) Å are elongated due to the anisobidentate attachment of the sulfur ligands. Cadmium ions thus have a greater tendency to adopt higher coordination numbers than zinc, which could account for some of the reactivity differences between the two elements in biological systems.

Introduction

In recent paper,[1] we showed that the zinc derivative of *cis*-1-methylthiostilbene-2-thiol, $Zn[Ph(SCH_3)C{=}C(S)Ph]_2$ and its adducts with 4-(dimethylamino)pyridine (dmapy) and 2,2'-bipyridyl (bpy) adopt pentacoordinated structures under conditions where tetra- and hexacoordinated geometries are possible. This observation may be relevant to the understanding of the functions of zinc in enzymes and in other biologically important zinc complexes in which zinc is usually assumed to be tetracoordinated. While this is often true for the resting states of the enzymes, it need not necessarily be the case, especially not in their functional states. Thus, in enzymes such as carbonic anhydrase[2] and in liver alcohol dehydrogenase,[3] zinc has been assumed to be pentacoordinated. Complexes of zinc with coordination numbers higher than 4 may also be formed in the interactions of the complexed zinc ions in the RNA and DNA polymerases with the base components of the nucleic acids.[4] Much of this evidence was obtained through studies of the enzymes in which zinc was substituted by cobalt[5] or cadmium[6] and from work with model compounds of these elements. In the previously investigated complexes with simple thiolato and nitrogen ligands, tetracoordination predominated, but the number of cases investigated is still relatively small. We therefore decided to synthesize the cadmium derivatives of *cis*-1-methylthiostilbene-2-thiol and of their adducts with dmapy and bpy and to compare their structures with those of the corresponding zinc compounds.

In contrast to the dimeric Zn derivative, the corresponding Cd complex of composition $Cd[Ph(SCH_3)C{=}C(S)Ph]_2$ (**1**) was found to be only marginally soluble in common solvents, suggesting a polymeric structure. On reaction of **1** with dimethyl sulfoxide (DMSO), however, a crystalline adduct of composition $Cd[Ph(SCH_3)C{=}C(S)Ph]_2$ (DMSO) (**2**) was obtained which could be structurally characterized. In further contrast to the behavior

---

[†] Present address: Department of Chemistry, Sri Krishnadevaraya University, Anantapur, 515003 India.

[‡] Present address: Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

[§] University of Missouri.

[‖] University of California.

(1) Zhang, C.; Chadha, R.; Reddy, H. K.; Schrauzer, G. N. *Inorg. Chem.* **1991**, *30*, 3865.

(2) (a) Gupta, R. K.; Pesando, J. M. *J. Biol. Chem.* **1975**, *250*, 2630. (b) Kannan, K. K.; Pelef, M.; Fridbourg, K.; Cid-Dresner, M.; Lougren, S. *FEBS Lett.* **1977**, *73*, 115.

(3) Dworschach, R. T.; Plapp, B. V. *Biochemistry* **1977**, *16*, 2716.

(4) Wu, F. Y.-H.; Wu, Ch.-W. *Annu. Rev. Nutr.* **1987**, *7*, 251-272 and references cited therein.

(5) Corwin, D. T., Jr.; Fikar, R.; Koch, S. A. *Inorg. Chem.* **1987**, *26*, 3080.

(6) Corwin, D. T., Jr.; Gruff, E. S.; Koch, S. A. *J. Chem. Soc., Chem. Commun.* **1987**, 966.

of the corresponding Zn complex, which forms a pentacoordinate 1:1 adduct with dmapy,[1] the reaction of **1** with dmapy produced a 1:2 adduct of composition Cd[Ph(SCH$_3$)C=C(S)Ph]$_2$(dmapy)$_2$ (**3**), whose structure was also determined. Only the reaction of **1** with bpy afforded the expected 1:1 adduct, Cd[Ph(SCH$_3$)C=C(S)Ph]$_2$ (bpy) (**4**), in apparent analogy to the corresponding zinc complex. However, as will be shown in the following sections, its structure is completely different. The possible origins of these remarkable chemical and structural differences between these complexes of cadmium and zinc will be discussed.

Experimental Section

Synthesis of Cd[Ph(CH$_3$S)C=C(S)Ph]$_2$ (1) and Its DMSO Adduct (2). To a solution of 1.29 g (5 mmol) of *cis*-1-methylthiostilbene-2-thiol, prepared as described in ref 7, in 150 mL of hot ethanol, was added a solution of Cd(NO$_3$)$_2$·6H$_2$O, 0.77 g (2.5 mmol), in 5 mL of water dropwise and with constant stirring. A colorless amorphous precipitate formed immediately. The reaction mixture was cooled to room temperature, and the precipitate was collected and dried after washing with ethanol and *n*-hexane, to yield 1.40 g (2.45 mmol) of product, corresponding to a yield of 98% based on Cd(NO$_3$)$_2$·6H$_2$O; mp 222 °C dec. Anal. Calcd for C$_{30}$H$_{26}$S$_4$Cd (**1**): C, 63.02; H, 4.58; Cd, 19.66. Found: C, 62.79; H, 4.66; Cd, 19.58. The compound shows marginal solubility in common organic solvents and did not form single crystals. ^{1}H NMR (ppm) in CDCl$_3$: 2.04 (s, 12 H, SCH$_3$), 6.89–7.04 (m, 40 H, Ph). From hot solutions of **1** in DMSO, a crystalline 1:1 adduct (**2**), mp (sealed tube) 165 °C dec, precipitates on cooling. Anal. Calcd for C$_{32}$H$_{32}$S$_5$CdO: C, 54.51; H, 4.58; S, 22.70. Found: C, 54.57; H, 4.39; S, 22.85. ^{1}H NMR (ppm) in CD$_3$SOCD$_3$: 2.00 (s, 12 H, SCH$_3$), 3.31 (s, 12 H, CH$_3$SOCH$_3$), 6.94–7.10 (m, 40 H, Ph).

Synthesis of Cd[Ph(CH$_3$S)C=C(S)Ph]$_2$(dmapy)$_2$ (3). Complex **2**, 0.313 g (0.44 mmol), and dmapy, 0.305 g (2.8 mmol), were placed in a glass vial of 10-mL capacity. The vial was sealed and heated to 120 °C for 1 h. When the vial was cooled, a yellow precipitate formed, which was collected, washed several times with water, with ethanol, and finally with *n*-hexane, and dried. The compound was recrystallized from CH$_2$Cl$_2$–*n*-hexane (1:1), yielding 0.38 g (0.436 mmol), 99%, based on **2**; mp, 179 °C dec. ^{1}H NMR (ppm) in CDCl$_3$: 1.96 (s, 6 H, SCH$_3$), 3.01 (s, 12 H, N–CH$_3$), 6.94–7.06 (m, 20 H, Ph), 6.51 (s), 7.23 (d), and 8.32 (d) (8 H, Py). Anal. Calcd for C$_{44}$H$_{46}$S$_4$N$_4$Cd: C, 60.66; H, 5.28; S, 14.71. Found: C, 61.22; H, 5.35; S, 14.90.

Synthesis of Cd[Ph(CH$_3$S)C=C(S)Ph]$_2$(bpy) (4). Complex **2**, 0.626 g (0.89 mmol), and bpy, 0.39 g (2.5 mmol), were heated in a sealed glass vial of 10-mL capacity to 100 °C for 1 h. When the vial was cooled, a yellow precipitate formed, which was collected, washed several times with water, with ethanol, and finally with *n*-hexane, and dried. The compound was recrystallized from CH$_2$Cl$_2$–*n*-hexane (1:1). Yield: 0.70 g (0.81 mmol), 91% based on **2**. Mp: 188 °C dec. ^{1}H NMR (ppm) in CDCl$_3$: 2.30 (s, 6 H, S–CH$_3$), 6.92–7.12 (m, 20 H, Ph), 7.39 (q), 7.86 (d), 7.88 (d), 7.91 (d), 8.22 (d) and 8.78 (d) (8 H, bpy). Anal. Calcd for C$_{40}$H$_{34}$S$_4$N$_2$Cd: C, 61.50; H, 4.38; Cd, 14.39. Found: C, 61.76; H, 3.91; Cd, 14.1.

X-ray Crystallographic Structure Determinations of Complexes 2–4. Pale yellow prismatic crystals of complexes **2** and **3** and yellow prismatic crystals of complex **4** were obtained as described above and were found to be stable during X-ray analysis. Intensity data for crystals of **2** and **4** were obtained at 23 °C on an Enraf Nonius CAD 4 automatic diffractometer, using the $\theta/2\theta$ scan technique with Mo Kα radiation from a graphite monochromator (λ = 0.7093 Å). The approximate crystal dimensions for **2** were 0.10 × 0.10 × 0.20 mm and for **4** 0.25 × 0.30 × 0.30 mm, respectively. No absorption corrections were applied. Cell dimensions were obtained from 25 reflections with 2θ in the range 22–26°. For **2**, a total of 9514 reflections were measured, of which 8984 were unique. For **4**, the total number of reflections measured was 5280, of which 5013 were unique. Space groups, lattice parameters and other relevant information are given in Table I. The structures were solved by direct methods and refined using the full-matrix least-squares method. Intensity data of **3** were obtained at 25 °C on a Siemens R3m/V automatic diffractometer with Mo Kα radiation of λ = 0.71073 Å from a highly oriented graphite crystal monochromator. The approximate crystal dimensions were 0.20 × 0.20 × 0.25 mm. A semiempirical absorption correction using the Φ-scan technique (μ = 10.3 cm^{-1}) was employed. A total of 2664 reflections were collected of which 2372 were independent. The space group, lattice parameters, and additional information are given in Table I. The structure was solved using direct methods with full-matrix least-squares refinement, employing the Siemens SHELXTL PLUS (VMS) system. The hydrogen atoms were placed in positions according to the Riding model with fixed isotropic *U*. The final difference maps had no features of chemical significance.

Table I. Crystallographic Data Collection Parameters for Complexes **2–4**

	2 (DMSO adduct)	**3**	**4**
formula	C$_{32}$H$_{32}$S$_5$CdO	C$_{44}$H$_{46}$N$_4$S$_4$Cd	C$_{40}$H$_{34}$N$_2$S$_4$Cd
instrument	Enraf Nonius	Siemens R3m/V	Enraf Nonius
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$
a, Å	11.529 (4)	17.483 (4)	13.652 (3)
b, Å	12.995 (5)	12.291 (3)	12.843 (7)
c, Å	22.804 (8)	19.963 (5)	10.564 (2)
α, deg	106.480 (20)	90.0	101.39 (3)
β, deg	92.590 (20)	98.998 (20)	94.20 (2)
γ, deg	94.680 (20)	90.0	94.36 (3)
V, Å^3	3246.8 (20)	4289.7	1803.1 (11)
T, °C	23	25	23
d_{calcd}, g/cm^3	1.443	1.114	1.443
Z	4	4	2
fw	705.34	719.23	783.39
λ, Å	0.709 30	0.710 73	0.709 30
$2\theta_{max}$, deg	46	45	46
R^a	0.047	0.0414	0.037
$R_w{}^b$	0.069	0.0407	0.056
goodness of fit $(S)^c$	1.69	1.49	1.49

$^a R = (\sum||F_o| - |F_c||/\sum|F_o|)$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. $^c S = [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

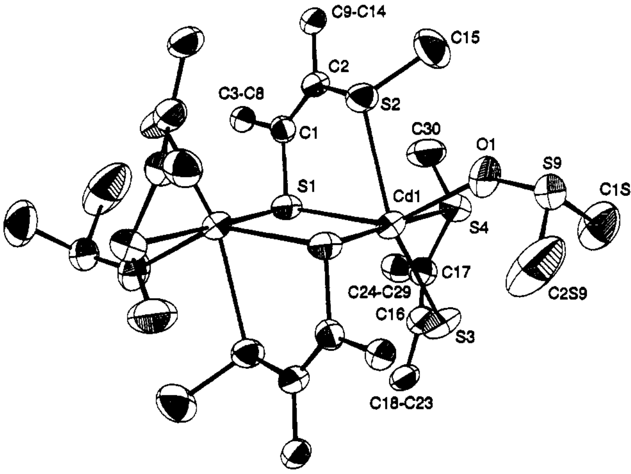

Figure 1. Perspective drawing of the structure of **2**, with numbering of atoms other than hydrogen.

Results

The cadmium derivative of *cis*-methylthiostilbenethiol (**1**), of composition Cd[Ph(CH$_3$S)C=C(S)Ph]$_2$, as obtained by the reaction of *cis*-methylthiostilbenethiol with cadmium nitrate in ethanol appears to have a polymeric structure but forms a crystalline 1:1 adduct with DMSO (**2**), which could be analyzed by X-ray crystallographic methods. Also prepared and structurally characterized were the adducts Cd[Ph(CH$_3$S)C=C(S)Ph]$_2$(dmapy)$_2$ (**3**) and Cd[Ph(CH$_3$S)C=C(S)Ph]$_2$ (bpy) (**4**). Crystallographic data collection parameters for complexes **2–4** are given in Table I; perspective drawings of the structures are shown in Figures 1–3. Selected positional parameters and geometrical data are given in Tables II–VII.

The compounds **2–4** contain hexacoordinated Cd ions in distorted octahedral environments. Compound **2** forms a centrosymmetric μ-S-bridged dimer in which each Cd ion is coordinated to five ligand sulfur atoms and one oxygen atom of DMSO. The lengths of the covalent Cd–S bond, Cd(1)–S(3), is 2.5072 (22) Å and the average lengths of the μ-Cd–S bonds, Cd(1)–S(1) and Cd(1)–S(1)a, of 2.652 (22) Å are within normal ranges; the Cd$_2$S$_4$ moiety is approximately rectangular, although Cd(2) is displaced

---

(7) Schrauzer, G. N.; Zhang, C.; Schlemper, E. O. *Inorg. Chem.* **1990**, *29*, 3371.

Table II. Atomic Parameters *x*, *y*, and *z* and B_{iso} for Complex **1**, Where Positions of H Atoms Are Not Shown and Esd's Refer to the Last Digit Printed

	x	*y*	*z*	B_{iso}, Å^2
Cd(1)	0.12740 (5)	0.42079 (5)	0.49893 (3)	3.46 (3)
Cd(2)	0.64105 (5)	0.58053 (5)	0.00646 (3)	3.49 (3)
S(1)	−0.07231 (17)	0.38846 (15)	0.43230 (9)	3.31 (9)
S(2)	−0.03617 (18)	0.33070 (17)	0.56247 (10)	3.75 (9)
S(3)	0.29717 (19)	0.45119 (20)	0.43886 (10)	4.59 (11)
S(4)	0.19117 (20)	0.21042 (18)	0.42030 (11)	4.44 (11)
S(5)	0.46534 (17)	0.59000 (16)	0.07849 (9)	3.50 (9)
S(6)	0.48073 (18)	0.69620 (17)	−0.03586 (10)	3.77 (10)
S(7)	0.80262 (19)	0.51665 (19)	0.06120 (10)	4.25 (10)
S(8)	0.76832 (20)	0.76925 (18)	0.09820 (11)	4.41 (11)
C(1)	−0.1627 (6)	0.2875 (6)	0.4536 (3)	2.9 (3)
C(2)	−0.1455 (6)	0.2587 (6)	0.5055 (3)	3.0 (3)
C(3)	−0.2609 (6)	0.2373 (6)	0.4066 (3)	3.1 (3)
C(4)	−0.3749 (8)	0.2430 (9)	0.4246 (4)	5.8 (6)
C(5)	−0.4675 (8)	0.1991 (10)	0.3812 (6)	7.7 (7)
C(6)	−0.4500 (9)	0.1495 (9)	0.3202 (6)	7.3 (6)
C(7)	−0.3368 (10)	0.1471 (8)	0.3037 (5)	6.5 (6)
C(8)	−0.2440 (8)	0.1906 (7)	0.3464 (4)	4.6 (4)
C(9)	−0.2189 (6)	0.1704 (6)	0.5199 (3)	3.2 (4)
C(10)	−0.2843 (7)	0.1941 (7)	0.5709 (4)	4.7 (4)
C(11)	−0.3539 (9)	0.1111 (9)	0.5837 (5)	6.4 (6)
C(12)	−0.3564 (9)	0.0063 (8)	0.5479 (5)	6.1 (6)
C(13)	−0.2875 (9)	−0.0167 (8)	0.4997 (5)	5.9 (5)
C(14)	−0.2193 (8)	0.0649 (6)	0.4854 (4)	4.5 (4)
C(15)	0.0227 (9)	0.2247 (9)	0.5887 (5)	6.4 (6)
C(16)	0.2515 (7)	0.3645 (6)	0.3667 (4)	3.7 (4)
C(17)	0.1984 (7)	0.2625 (6)	0.3564 (4)	3.8 (4)
C(18)	0.2804 (6)	0.4083 (7)	0.3144 (4)	3.8 (4)
C(19)	0.3472 (8)	0.3556 (8)	0.2688 (4)	4.9 (5)
C(20)	0.3852 (9)	0.4037 (10)	0.2237 (5)	7.1 (7)
C(21)	0.3522 (11)	0.5032 (10)	0.2245 (5)	8.0 (7)
C(22)	0.2812 (13)	0.5543 (9)	0.2678 (6)	8.8 (8)
C(23)	0.2480 (9)	0.5082 (7)	0.3129 (5)	5.7 (5)
C(24)	0.1395 (7)	0.1949 (6)	0.2962 (4)	4.1 (4)
C(25)	0.0485 (8)	0.2278 (7)	0.2712 (4)	5.0 (4)
C(26)	−0.0115 (9)	0.1657 (9)	0.2173 (5)	6.4 (6)
C(27)	0.0277 (12)	0.0694 (9)	0.1863 (5)	7.4 (7)
C(28)	0.1220 (10)	0.0354 (8)	0.2098 (5)	6.6 (6)
C(29)	0.1795 (9)	0.0968 (7)	0.2638 (5)	5.6 (5)
C(30)	0.0753 (9)	0.1020 (8)	0.3979 (5)	6.0 (5)
C(31)	0.3830 (6)	0.6945 (6)	0.0699 (3)	2.9 (3)
C(32)	0.3897 (7)	0.7420 (6)	0.0246 (4)	3.6 (4)
C(33)	0.2985 (6)	0.7240 (6)	0.1183 (4)	3.4 (4)
C(34)	0.3381 (7)	0.7768 (7)	0.1784 (4)	4.4 (4)
C(35)	0.2598 (9)	0.8007 (8)	0.2238 (4)	5.4 (5)
C(36)	0.1422 (9)	0.7692 (8)	0.2092 (5)	5.8 (5)
C(37)	0.1036 (8)	0.7171 (8)	0.1516 (5)	6.2 (6)
C(38)	0.1794 (7)	0.6943 (7)	0.1048 (4)	4.7 (5)
C(39)	0.3163 (7)	0.8287 (6)	0.0178 (4)	3.9 (4)
C(40)	0.3056 (9)	0.9196 (7)	0.0660 (5)	5.5 (5)
C(41)	0.2318 (10)	0.9988 (8)	0.0577 (6)	7.1 (6)
C(42)	0.1766 (9)	0.9843 (10)	0.0005 (6)	7.7 (7)
C(43)	0.1857 (9)	0.8940 (9)	−0.0469 (6)	7.1 (7)
C(44)	0.2548 (9)	0.8190 (8)	−0.0379 (5)	6.0 (6)
C(45)	0.5508 (10)	0.8179 (9)	−0.0469 (5)	6.9 (6)
C(46)	0.7846 (6)	0.5913 (6)	0.1367 (3)	3.2 (4)
C(47)	0.7645 (7)	0.6972 (6)	0.1540 (4)	3.7 (4)
C(48)	0.7964 (7)	0.5306 (6)	0.1834 (4)	3.5 (4)
C(49)	0.7214 (8)	0.4393 (7)	0.1794 (4)	4.6 (4)
C(50)	0.7336 (9)	0.3819 (8)	0.2217 (5)	6.0 (5)
C(51)	0.8190 (9)	0.4131 (8)	0.2672 (4)	5.5 (5)
C(52)	0.8944 (8)	0.5015 (8)	0.2715 (4)	5.6 (5)
C(53)	0.8821 (7)	0.5604 (8)	0.2306 (4)	4.8 (5)
C(54)	0.7381 (7)	0.7566 (6)	0.2161 (4)	3.8 (4)
C(55)	0.8088 (9)	0.8473 (7)	0.2523 (5)	5.8 (5)
C(56)	0.7800 (11)	0.9027 (9)	0.3078 (5)	7.2 (6)
C(57)	0.6765 (12)	0.8751 (9)	0.3301 (4)	7.7 (7)
C(58)	0.6039 (10)	0.7845 (10)	0.2957 (5)	7.0 (6)
C(59)	0.6373 (9)	0.7256 (7)	0.2392 (4)	5.3 (5)
C(60)	0.6723 (9)	0.8744 (8)	0.1271 (5)	6.0 (6)
O(1)	0.2330 (5)	0.3805 (5)	0.5793 (3)	5.5 (3)
S(9)	0.3476 (3)	0.4079 (3)	0.61636 (16)	4.73 (16)
S(9′)	0.3676 (6)	0.4396 (6)	0.5765 (3)	4.16 (14)
C(1S(9))	0.4475 (9)	0.3303 (8)	0.5608 (6)	7.2 (6)
C(2S(9))	0.3960 (11)	0.5378 (11)	0.6154 (8)	10.8 (9)
O(3)	0.7497 (5)	0.6481 (5)	−0.0623 (3)	5.1 (3)
S(10)	0.8674 (3)	0.6032 (3)	−0.07700 (18)	6.57 (19)
S(10′)	0.8653 (15)	0.6873 (13)	−0.0771 (8)	7.4 (4)
C(1S(10))	0.9714 (9)	0.6926 (12)	−0.0236 (6)	8.7 (8)
C(2S(10))	0.9133 (12)	0.6433 (19)	−0.1414 (6)	15.6 (16)

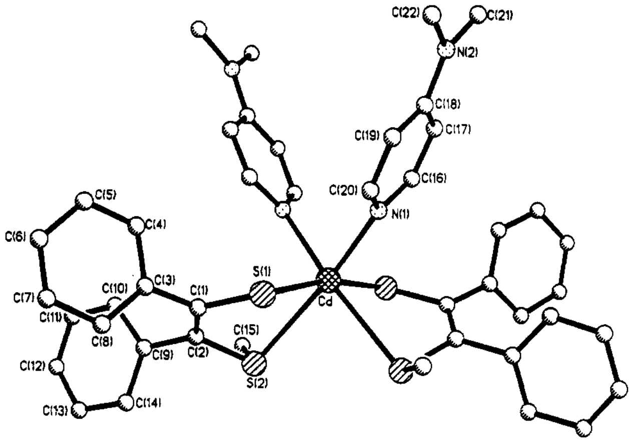

Figure 2. Perspective drawing of **3**, with numbering of atoms other than hydrogen.

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for Complex **3**, Excepting Hydrogen Atoms

	x	*y*	*z*	*U*(eq)[a]
Cd	0	3131 (1)	2500	49 (1)
S(1)	1453 (1)	3349 (1)	2900 (1)	62 (1)
S(2)	515 (1)	4866 (1)	1718 (1)	59 (1)
N(1)	−27 (3)	1747 (3)	3333 (2)	64 (2)
N(2)	−69 (3)	−1232 (4)	4333 (3)	81 (2)
C(1)	1799 (3)	3664 (4)	2146 (2)	49 (2)
C(2)	1428 (3)	4286 (4)	1640 (2)	47 (2)
C(3)	2590 (3)	3229 (5)	2107 (2)	51 (2)
C(4)	2725 (3)	2114 (6)	2083 (3)	83 (3)
C(5)	3436 (4)	1701 (6)	2025 (3)	85 (3)
C(6)	4039 (4)	2369 (8)	2006 (3)	90 (3)
C(7)	3937 (4)	3457 (7)	2045 (3)	93 (3)
C(8)	3211 (3)	3892 (5)	2082 (3)	71 (2)
C(9)	1743 (3)	4564 (5)	1009 (3)	53 (2)
C(10)	1866 (3)	3776 (5)	545 (3)	62 (2)
C(11)	2107 (3)	4056 (7)	−52 (3)	93 (3)
C(12)	2255 (4)	5089 (9)	−202 (4)	107 (4)
C(13)	2163 (4)	5880 (7)	256 (4)	109 (4)
C(14)	1901 (3)	5628 (6)	868 (3)	81 (3)
C(15)	−30 (3)	4665 (6)	894 (3)	90 (3)
C(16)	−650 (3)	1105 (5)	3267 (3)	76 (3)
C(17)	−696 (3)	144 (5)	3591 (3)	73 (3)
C(18)	−63 (3)	−256 (5)	4025 (3)	64 (2)
C(19)	587 (3)	423 (5)	4110 (3)	66 (2)
C(20)	574 (3)	1382 (5)	3766 (3)	67 (2)
C(21)	−736 (4)	−1939 (5)	4209 (4)	111 (3)
C(22)	611 (4)	−1688 (5)	4726 (3)	102 (3)

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

by 0.426 Å out of the S(1)Cd(1)S(1a) plane. The two coordinate Cd–S bonds, Cd(1)–S(2) and Cd(1)–S(4), of 2.8045 (22) and 2.976 (3) Å, respectively, are relatively long, but the angles of the bonds around these sulfur atoms are nearly tetrahedral, consistent with the presence of genuine coordinate bonds to Cd. In **3**, the dmapy ligands are in nearly rectangular cis positions opposite to elongated coordinate Cd–S bonds with average lengths of 2.868 (2) Å. The axial covalent Cd–S bonds are of normal length. In **4**, the coordination of bpy to Cd is slightly asymmetrical, with Cd–N bond distances of 2.346 (4) and 2.418 (3) Å, respectively. One of the two equidistant covalent Cd–S bonds is in a nearly perpendicular axial position relative to the Cd–bpy moiety, the other is in a distorted equatorial position with a S–Cd–N bond angle of 156.92 (9)°. One of the two coordinate Cd–S bonds of 2.8151 (19) Å is in the axial position, with other in a distorted equatorial position.

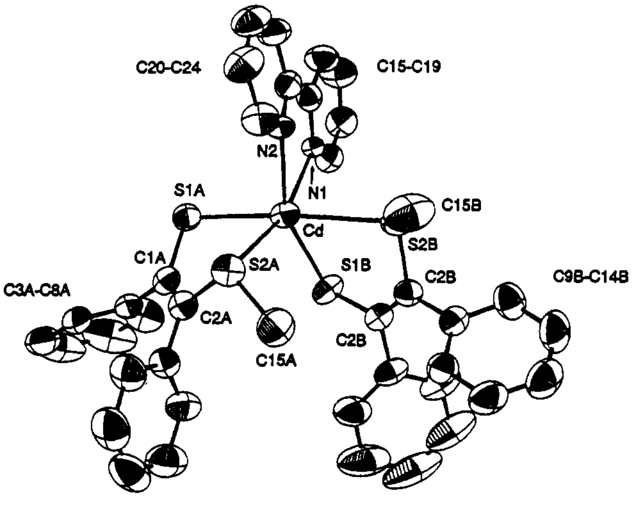

Figure 3. Perspective drawing of **4**, with numbering of atoms other than hydrogen.

Table IV. Atomic Parameters *x*, *y*, and *z* and B_{iso} for Complex **4**, Excepting Hydrogen Atoms Where Esd's Refer to the Last Digit Printed

	x	*y*	*z*	B_{iso}, Å^2
Cd	0.305187 (21)	0.331811 (23)	0.21395 (3)	3.744 (15)
S(1A)	0.45906 (8)	0.23824 (9)	0.17042 (12)	4.28 (5)
S(2A)	0.23613 (9)	0.13421 (10)	0.05269 (11)	4.36 (5)
C(1A)	0.4130 (3)	0.1069 (3)	0.1722 (4)	3.62 (17)
C(2A)	0.3214 (3)	0.0628 (3)	0.1279 (4)	3.71 (18)
C(3A)	0.4875 (3)	0.0446 (3)	0.2250 (4)	3.72 (18)
C(4A)	0.5288 (4)	0.0773 (5)	0.3501 (5)	6.2 (3)
C(5A)	0.6008 (6)	0.0204 (7)	0.3974 (8)	9.4 (5)
C(6A)	0.6333 (5)	−0.0660 (7)	0.3177 (11)	9.0 (5)
C(7A)	0.5913 (5)	−0.0993 (5)	0.1966 (8)	6.9 (4)
C(8A)	0.5178 (4)	−0.0454 (4)	0.1482 (5)	5.12 (23)
C(9A)	0.2849 (3)	−0.0486 (3)	0.1315 (4)	4.04 (19)
C(10A)	0.2641 (4)	−0.1237 (4)	0.0170 (5)	5.9 (3)
C(11A)	0.2278 (5)	−0.2263 (5)	0.0192 (8)	7.6 (4)
C(12A)	0.2156 (5)	−0.2553 (5)	0.1357 (10)	8.0 (4)
C(13A)	0.2347 (5)	−0.1809 (5)	0.2497 (7)	7.1 (4)
C(14A)	0.2700 (4)	−0.0774 (4)	0.2473 (5)	4.93 (22)
C(15A)	0.1209 (4)	0.0905 (5)	0.1084 (6)	6.4 (3)
S(1B)	0.26403 (8)	0.30239 (11)	0.43427 (11)	4.43 (5)
S(2B)	0.11761 (9)	0.41586 (11)	0.25569 (12)	4.67 (6)
C(1B)	0.1353 (3)	0.2915 (3)	0.4324 (4)	3.76 (18)
C(2B)	0.0709 (3)	0.3315 (3)	0.3562 (4)	3.66 (17)
C(3B)	0.1012 (3)	0.2334 (4)	0.5328 (4)	4.36 (21)
C(4B)	0.0513 (4)	0.2839 (5)	0.6340 (5)	6.6 (3)
C(5B)	0.0234 (5)	0.2347 (9)	0.7294 (7)	9.2 (5)
C(6B)	0.0430 (6)	0.1291 (11)	0.7226 (10)	11.6 (7)
C(7B)	0.0914 (6)	0.0773 (8)	0.6225 (11)	10.9 (6)
C(8B)	0.1222 (4)	0.1298 (5)	0.5285 (6)	6.6 (3)
C(9B)	−0.0378 (3)	0.3154 (4)	0.3574 (4)	3.93 (19)
C(10B)	−0.0852 (3)	0.2148 (4)	0.3282 (5)	4.49 (22)
C(11B)	−0.1866 (4)	0.1993 (5)	0.3318 (6)	5.9 (3)
C(12B)	−0.2400 (4)	0.2837 (6)	0.3659 (6)	6.7 (3)
C(13B)	−0.1948 (4)	0.3833 (5)	0.3972 (7)	6.6 (3)
C(14B)	−0.0927 (4)	0.4015 (4)	0.3892 (5)	5.46 (25)
C(15B)	0.0284 (5)	0.3839 (6)	0.1126 (6)	8.0 (4)
N(1)	0.38097 (24)	0.5066 (3)	0.2763 (3)	2.28 (13)
N(2)	0.3067 (3)	0.4196 (3)	0.0315 (3)	2.65 (15)
C(15)	0.3969 (3)	0.5633 (3)	0.1862 (4)	3.75 (19)
C(16)	0.4461 (4)	0.6652 (4)	0.2200 (5)	5.5 (3)
C(17)	0.4783 (4)	0.7069 (4)	0.3472 (5)	6.1 (3)
C(18)	0.4614 (4)	0.6473 (4)	0.4399 (5)	5.33 (23)
C(19)	0.4115 (3)	0.5464 (4)	0.3987 (4)	4.38 (20)
C(20)	0.3621 (3)	0.5132 (4)	0.0509 (4)	3.79 (18)
C(21)	0.3889 (4)	0.5595 (4)	−0.0508 (5)	4.86 (23)
C(22)	0.3545 (4)	0.5056 (5)	−0.1792 (5)	5.9 (3)
C(23)	0.2975 (4)	0.4121 (5)	−0.1977 (4)	5.8 (3)
C(24)	0.2741 (4)	0.3705 (4)	−0.0900 (5)	5.15 (23)

Table V. Selected Geometric Data for **2**

	Distances (Å)		
Cd(1)–S(1)	2.6364 (22)	S(2)–C(2)	1.766 (8)
Cd(1)–S(1)a	2.6677 (23)	S(2)–C(15)	1.812 (10)
Cd(1)–S(2)	2.8045 (22)	S(3)–C(16)	1.739 (8)
Cd(1)–S(3)	2.5072 (22)	S(4)–C(17)	1.773 (8)
Cd(1)–S(4)	2.976 (3)	S(4)–C(30)	1.801 (10)
Cd(1)–O(1)	2.358 (6)	S(5)–Cd(2)b	2.6557 (24)
Cd(2)–S(5)	2.6540 (22)	S(5)–C(31)	1.765 (7)
Cd(2)–S(5)b	2.6557 (24)	S(6)–C(32)	1.767 (8)
Cd(2)–S(6)	2.7757 (22)	S(6)–C(45)	1.800 (10)
Cd(2)–S(7)	2.5181 (23)	S(7)–C(46)	1.749 (8)
Cd(2)–S(8)	2.957 (3)	S(8)–C(47)	1.780 (8)
Cd(2)–O(3)	2.360 (5)	S(8)–C(60)	1.821 (10)
S(1)–Cd(1)a	2.6677 (23)	C(1)–C(2)	1.350 (10)
S(1)–C(1)	1.793 (7)	C(16)–C(17)	1.362 (11)
	Angles (deg)		
S(1)–Cd(1)–S(1)a	91.16 (7)	S(5)b–Cd(2)–S(6)	84.97 (7)
S(1)–Cd(1)–S(2)	74.02 (6)	S(5)b–Cd(2)–S(7)	107.96 (8)
S(1)–Cd(1)–S(3)	111.76 (8)	S(5)b–Cd(2)–S(8)	177.62 (6)
S(1)–Cd(1)–S(4)	88.81 (7)	S(5)b–Cd(2)–O(3)	95.48 (16)
S(1)–Cd(1)–O(1)	146.10 (15)	S(6)–Cd(2)–S(7)	167.07 (7)
S(1)a–Cd(1)–S(2)	85.52 (7)	S(6)–Cd(2)–S(8)	96.01 (7)
S(1)a–Cd(1)–S(3)	109.07 (7)	S(6)–Cd(2)–O(3)	78.39 (15)
S(1)a–Cd(1)–S(4)	178.73 (6)	S(7)–Cd(2)–S(8)	71.07 (7)
S(1)a–Cd(1)–O(1)	94.99 (17)	S(7)–Cd(2)–O(3)	99.82 (15)
S(2)–Cd(1)–S(3)	163.72 (8)	S(8)–Cd(2)–O(3)	82.61 (16)
S(2)–Cd(1)–S(4)	95.69 (7)	Cd(1)–S(1)–Cd(1)a	88.84 (7)
S(2)–Cd(1)–O(1)	73.29 (15)	Cd(1)–S(1)–C(1)	107.25 (24)
S(3)–Cd(1)–S(4)	69.78 (7)	Cd(1)a–S(1)–C(1)	106.22 (24)
S(3)–Cd(1)–O(1)	97.61 (16)	Cd(1)–S(2)–C(2)	104.54 (25)
S(4)–Cd(1)–O(1)	85.73 (17)	Cd(1)–S(2)–C(15)	110.9 (4)
S(5)–Cd(2)–S(5)b	92.53 (7)	C(2)–S(2)–C(15)	102.9 (4)
S(5)–Cd(2)–S(6)	74.31 (6)	Cd(1)–S(3)–C(16)	101.1 (3)
S(5)–Cd(2)–S(7)	104.39 (7)	Cd(1)–S(4)–C(17)	90.9 (3)
S(5)–Cd(2)–S(8)	89.83 (7)	Cd(1)–S(4)–C(30)	115.9 (4)
S(5)–Cd(2)–O(3)	150.70 (16)	C(17)–S(4)–C(30)	104.5 (4)
		Cd(2)–S(5)–Cd(2)b	87.47 (7)

Table VI. Selected Geometric Data for **3**

	Distances (Å)		
Cd–S(1)	2.556 (1)	Cd–S(2)	2.868 (2)
Cd–N(1)	2.384 (4)	Cd–S(1A)	2.556 (1)
Cd–S(2A)	2.869 (2)	Cd–N(1A)	2.384 (4)
S(1)–C(1)	1.752 (5)	S(2)–C(2)	1.778 (5)
S(2)–C(15)	1.784 (5)	N(1)–C(16)	1.335 (7)
N(1)–C(20)	1.330 (7)	N(2)–C(18)	1.349 (8)
N(2)–C(21)	1.444 (9)	N(2)–C(22)	1.432 (8)
C(1)–C(2)	1.348 (6)		
	Angles (deg)		
S(1)–Cd–S(2)	73.2 (1)	S(1)–Cd–N(1)	89.1 (1)
S(2)–Cd–N(1)	162.1 (1)	S(1)–Cd–S(1A)	168.0 (1)
S(2)–Cd–S(1A)	97.7 (1)	N(1)–Cd–S(1A)	99.5 (1)
S(1)–Cd–S(2A)	97.7 (1)	S(2)–Cd–S(2A)	84.0 (1)
N(1)–Cd–S(2A)	96.2 (1)	S(1A)–Cd–S(2A)	73.2 (1)
S(1)–Cd–N(1A)	99.5 (1)	S(2)–Cd–N(1A)	96.3 (1)
N(1)–Cd–N(1A)	88.9 (2)	S(1A)–Cd–N(1A)	89.1 (1)
S(2A)–Cd–N(1A)	162.1 (1)	Cd–S(1)–C(1)	102.4 (1)
Cd–S(2)–C(2)	96.5 (2)	Cd–S(2)–C(15)	103.4 (2)
C(2)–S(2)–C(15)	102.8 (2)	Cd–N(1)–C(16)	117.3 (3)
Cd–N(1)–C(20)	126.5 (4)		

Discussion

Until recently, the thiolate chemistry of Cd(II) was believed to be characterized exclusively by tetrahedral coordination,[8] and hexacoordinated structures were observed only with special ligands such as the dithiocarbamates and dithiophosphates.[9] The present study shows that the anion of *cis*-1-methylthiostilbene-2-thiol, a facultative mono- and bidentate ligand, forms hexacoordinated complexes under conditions where zinc reached only coordination number 5.[1] With simple thiolato ligands several examples of isostructural tetracoordinated anionic complexes of the two elements have been reported.[8,9] The anions $[M_2(SR)_6]^{2-}$ (M = Zn, Cd; R = Et, Ph), for example, exhibit μ-S-bridged structures with

---

(8) Swenson, D.; Baenzinger, N. C.; Coucouvanis, D. *J. Am. Chem. Soc.* **1978**, *100*, 1934.

(9) Abrahams, J. I.; Garner, D. *J. Chem. Soc., Dalton Trans.* **1987**, 1577.

Table VII. Selected Geometric Data for **4**

	Distances (Å)		
Cd–S(1A)	2.5250 (14)	S(2A)–C(15A)	1.808 (6)
Cd–S(2A)	2.8151 (19)	C(1A)–C(2A)	1.344 (6)
Cd–S(1B)	2.5263 (12)	S(1B)–C(1B)	1.750 (4)
Cd–N(1)	2.346 (4)	S(2B)–C(2B)	1.776 (4)
Cd–N(2)	2.418 (3)	S(2B)–C(15B)	1.829 (6)
S(1A)–C(1A)	1.759 (4)	C(1B)–C(2B)	1.348 (6)
S(2A)–C(2A)	1.773 (4)		
	Angles (deg)		
S(1A)–Cd–S(2A)	75.60 (5)	S(1B)–Cd–N(2)	156.92 (9)
S(1A)–Cd–S(1B)	104.96 (5)	N(1)–Cd–N(2)	68.89 (12)
S(1A)–Cd–N(1)	97.73 (9)	Cd–S(1A)–C(1A)	99.56 (15)
S(1A)–Cd–N(2)	96.22 (9)	Cd–S(2A)–C(2A)	93.72 (14)
S(2A)–Cd–S(1B)	102.03 (5)	Cd–S(2A)–C(15A)	107.29 (21)
S(2A)–Cd–N(1)	159.17 (8)	C(2A)–S(2A)–C(15A)	102.11 (25)
S(2A)–Cd–N(2)	91.93 (9)	S(1A)–C(1A)–C(2A)	125.5 (4)
S(1B)–Cd–N(1)	98.76 (9)	S(1A)–C(1A)–C(3A)	113.2 (3)

essentially planar M_2S_2 moieties.[10] The cadmium ions are also tetracoordinate in the neutral thiophenolate, Cd$(SPh)_2$, which has a polymeric structure consisting of $Cd_4(SPh)_6$ units forming adamantane-like cages, each of which is linked by Cd–μ-SPh bonds to four adjacent cages.[11] The bis(cis-methylthiostilbenethiolate) of cadmium, Cd[Ph(SCH_3)C═C(S)Ph]$_2$ (**1**), also appears to have a polymeric structure. The coordination number of Cd in **1** is not known but is more likely 6 than 4 since the dimer of **2** exhibits a hexacoordinated structure with two coordinative Cd–O bonds due to the presence of the coordinated DMSO molecules. The Cd–μ-S bonds and the terminal Cd–S bonds are within the ranges observed in dimeric μ-S-bridged $Cd_2(SR)_6^{2-}$ anions,[10] and the dimensions of the Cd_2S_2 moieties are also closely the similar, although there is deviation from planarity in **2**. The two terminal coordinate Cd–S bonds of 2.8045 (22) and 2.976 (3) Å are long and evidently weak but still substantially shorter than the sum of the van der Waals radii of Cd and S (3.40 Å).[12] The sulfur ligands in **2** thus are bound in an anisobidentate fashion, but the coordination number of Cd is appropriately referred to as 6.

The Cd atom is also hexacoordinate in **3**, although it was previously found to be tetracoordinate in other complexes with S and N ligation. For example, a distorted tetrahedral structure has been reported[13] for the bis(methylimidazole) adduct of the 2,4,6-triisopropylthiophenolate of composition Cd(S-2,4,6-$Pr^i_3C_6H_2)_2$(1Me-imid)$_2$ (**5**). Evidently, in **5**, the tendency toward penta- or hexacoordination is suppressed by steric and electronic ligand effects. The mean Cd–S and Cd–N bond distances of 2.556 (1) and 2.384 (4) Å in **3** are longer than the corresponding bonds in **5** of 2.46 (1) and 2.28 (1) Å. The two equidistant coordinate Cd–S bonds of 2.869 (2) Å in **3** are intermediate in length between the two coordinate Cd–S bonds in **2**. In the bpy adduct **4**, the presence of the two coordinative Cd–S bonds in **4** contrasts with the corresponding Zn derivative in which only one ligand SCH_3 moiety is weakly coordinated and the other is in a noninteractive position. Cadmium probably has a preference for hexacoordination primarily due to its greater ionic radius (1.09 Å, for coordination number 6) relative to Zn^{2+} (0.82 Å, coordination number 5).[14] This difference in size causes an increase of the lengths of the Cd–S and Cd–N bonds compared to those involving Zn, which for the Cd–S bonds averages 0.234 Å and for the Cd–N(bpy) bonds, 0.298 Å. Accordingly, the increased tendency of Cd to form higher coordinated compounds than Zn may have to be considered to account for the different activities or structures of some of the Cd analogues of Zn enzymes or proteins.

Acknowledgment. We appreciate the National Science Foundation for their support.

Registry No. **1**, 139759-43-6; **2**, 139759-44-7; **3**, 139759-45-8; **4**, 139759-46-9.

Supplementary Material Available: For complexes **2–4**, tables of experimental details, positional parameters, anisotropic thermal parameters, bond distances, and bond angles and a figure showing a different view of **2** (23 pages); listings of observed and calculated structure factors (43 pages). Ordering information is given on any current masthead page.

---

(10) McCleverty, J. A.; Gill, S.; Kowalski, R. S. Z.; Bailey, N. A.; Adams, H.; Lumbard, K. W.; Murphy, M. A. *J. Chem. Soc., Dalton Trans.* **1982**, 493.

(11) Craig, D.; Dance, I. G.; Garbutt, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 165.

(12) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(13) Corwin, D. T., Jr.; Gruff, E. S.; Koch, S. A. *J. Chem. Soc., Chem. Commun.* **1987**, 966.

(14) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.