duction (Me_2SO) of **1** exhibit four hyperfine lines, consistent with the interaction of the odd electron with just one copper center ($I = {}^3/_2$). In the case of the oxidized species, the copper(III) centers would appear to be low spin. Compound **2** exhibits a clearly resolved four-line spectrum at room temperature on one-electron reduction (CH_3CN, Figure 5) and a poorly resolved four-line spectrum (CH_3CN) on one-electron oxidation. Again, in both cases, the odd electron is localized on one copper center. This behavior contrasts with that of **3**, where at room temperature (CH_2Cl_2 or CH_3CN) seven-line EPR spectra are obtained for the one-electron-reduced species, indicative of interaction of the odd electron with both copper centers.[22]

Oxidation of mononuclear copper(II) species to copper(III),[20,23] the one-electron oxidation of a trinuclear copper(II) system,[24] and the oxidation of a noncoupled binuclear copper(II) system by two one-electron steps[25] have been reported. However, complex **1** represents the first example of a magnetically coupled macrocyclic binuclear copper(II) system that involves two successive one-electron oxidation steps to produce Cu(II)–Cu(III) and Cu(III)–Cu(III) species as well as successive one-electron reduction steps to produce mixed-valence Cu(II)–Cu(I) species and binuclear Cu(I) species.

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Supplementary Material Available: Listings of anisotropic thermal parameters for **1** (Table SI) and bond lengths and bond angles pertaining to the ligands in **1** (Table SIII) (2 pages); a table of observed and calculated structure factors for **1** (Table SII) (15 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of Sulfonylurea Complexes with Cd^{2+}, Hg^{2+}, and Ag^+. Crystal and Molecular Structures of $K[Cd(chlorpropamide)_3]$ and $Hg(tolbutamide)_2$

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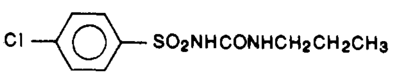
The synthesis and characterization of Cd^{2+}, Ag^+, and Hg^{2+} complexes with deprotonated tolbutamide and chlorpropamide ligands is described. The crystal and molecular structures of $Hg(CH_3C_6H_4SO_2NCONH\text{-}n\text{-}Bu)_2$ (I) and $K[Cd(ClC_6H_4SO_2NCONH\text{-}n\text{-}Pr)_3]$ (III) are reported. In I the coordination environment around the Hg^{2+} atom is strictly linear and the sulfonylurea ligand is bound in a predominantly monodentate fashion. The tolbutamide ligand is bound through the deprotonated sulfamido nitrogen atom. The Hg–N distance is 2.052 (17) Å. By comparison the chlorpropamide ligand is coordinated to a Cd^{2+} atom in a bidentate mode with both the sulfamido nitrogen and the carbonyl oxygen atoms bound to the metal center. The coordination environment around the Cd^{2+} atom can be best described as trigonal prismatic. The mean Cd–N and Cd–O distances are 2.212 (20) and 2.535 (24) Å, respectively. The counterion K^+ slightly interacts with the oxygen of the carbonyl and sulfonyl groups in the anion in such a way as to form a polymeric zigzag K···Cd chain parallel to the *a* axis. The IR spectra show (C$\overset{\cdot\cdot}{-}$O) and (C$\overset{\cdot\cdot}{-}$N) stretching frequencies, characteristic for either mode of sulfonylurea ligand coordination. On the basis of the IR spectra we propose a structure for $K[Ag(p\text{-}XC_6H_4SO_2NCONHR)_2]$ (tolbutamide, X = CH_3 and R = *n*-Bu; chlorpropamide, X = Cl and R = *n*-Pr) similar to that of the Hg^{2+} complexes. The ^1H NMR spectra of these compounds are also reported.

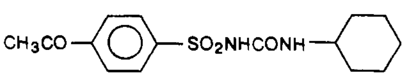
Introduction

Interest in the sulfonylurea class of compounds arises primarily from their ability to reduce blood sugar levels without affecting glucose tolerance.[1] Currently in the United States three sulfonylureas[2] are in use clinically for the management of maturity-onset or stable diabetes. These are *N*-((butylamino)carbonyl)-4-methylbenzenesulfonamide (tolbutamide, A), *N*-((propylamino)carbonyl)-4-chlorobenzenesulfonamide (chlorpropamide, B), and *N*-((cyclohexylamino)carbonyl)-4-acetylbenzenesulfonamide (acetohexamide, C). In addition to these, hundreds of (arylsulfonyl)ureas and related compounds have been synthesized and tested for hypoglycemic activity. The principal mechanism of the hypoglycemic action of the sulfonylureas is stimulation of insulin release by the β-cells of the pancreas.[3a] Generally these drugs induce increase in the insulin levels. In some cases however decrease has been observed.[3b,c] A divalent metal, Zn^{2+}, has been implicated in the release mechanism of insulin and has been found to occur in increased levels in the pancreas. The details of either sulfonylurea drug action and Zn^{2+} involvement or a possible mechanistic relationship between the two in insulin release remain unknown. Furthermore, there has been interest recently in whether

A (tolbutamide)



B (chlorpropamide)



C (acetohexamide)

[†] University of Thessaloniki.

[‡] University of Michigan.

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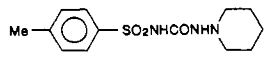
[2] A related compound is also used: 1-(hexahydro-1*H*-azepin-1-yl)-3-(*p*-toluenesulfonyl)urea (tolazamide)



This compound although usually classed as a sulfonylurea is actually a sulfonylsemicarbazide.

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and how drug–metal interactions may affect drug delivery to target cells.[4]

We have initiated studies on the coordination chemistry of sulfonylurea drugs with transition-metal and d^{10} metal ions in an attempt to examine their mode of binding and eventually how they affect drug delivery. In this paper we report our preliminary results with the divalent Cd^{2+} and Hg^{2+} and the monovalent Ag^+ ions. Progress with the Zn analogues will be reported later. The preparation and spectroscopic and crystal structural characterization of their tolbutamide and chlorpropamide complexes is described. The Hg^{2+} and Cd^{2+} complexes were reported previously but were poorly characterized and erroneously formulated.[5] The complexes described here are the first structurally characterized examples of compounds containing a sulfonyl urea ligand.

Experimental Section

Synthesis. The chemicals in this research were used as purchased. Dimethylformamide (DMF) was stored over 4A Linde molecular sieves for 24 h and then distilled under reduced pressure at 40 °C. Acetonitrile (CH_3CN) was distilled from calcium hydride (CaH_2) before use. Diethyl ether, anhydrous grade, and absolute ethanol were used without any further purification. The chlorpropamide and Tolbutamide were obtained from Pfizer and Hoechst Co., respectively. $Hg(CH_3COO)_2$ and $Cd(CH_3COO)_2$ were purchased from Merck Co.

Physical Methods. FT-IR spectra were obtained on an SX60 Nicolet Fourier transform spectrometer by using KBr pellets of the compounds. Proton NMR spectra were obtained on a Bruker 360 Pulse FT-NMR spectrometer with Me_4Si as internal standard. Chemical shifts are reported in parts per million (ppm). The powder diffraction diagrams were obtained by using a 114-mm-diameter Debye–Scherrer type camera with Ni-filtered Cu Kα radiation (λ = 1.5418 Å). Mass spectra were obtained on a Finnigan mass spectrometer. C, H, and N elemental analyses were performed on a Perkin-Elmer 240B elemental analyzer.

Preparation of Compounds. Mercury Bis[*N*-((butylamino)carbonyl)-4-methylbenzenesulfonamide], $Hg(CH_3C_6H_4SO_2NCONH\text{-}n\text{-}C_4H_9)_2$ (I). To a 80-mL solution of 60 mmol of tolbutamide and 60 mmol of KOH in absolute ethanol was added a suspension of 30 mmol of $Hg(CH_3COO)_2$ in 50 mL of absolute ethanol. The initial white precipitate dissolved with stirring. When the mixture was stirred for ca. 20 min. a white microcrystalline product started to separate. Further cooling to −10 °C afforded a white microcrystalline material, which was collected by filtration, washed with ethanol and diethyl ether, and dried in vacuo. Yield: 60–75% based on metal. Anal. Calcd for $C_{24}H_{34}N_4O_6S_2Hg$ (M_r = 739.27): C, 38.95; H, 4.60, N, 7.58; Hg, 27.10. Found: C, 37.96; H, 4.61; N, 7.42; Hg, 26.85. X-ray powder pattern spacings (Å): 23.9 (vs), 11.0 (vw), 9.0 (vw), 7.0 (m), 6.10 (m), 4.60 (s), 4.2 (vw), 4.0 (s), 3.75 (w), 3.35 (w), 3.15 (m), 3.05 (w), 2.90 (w), 2.80 (m).

Mercury Bis[*N*-((propylamino)carbonyl)-4-chlorobenzenesulfonamide], $Hg(ClC_6H_4SO_2NCONH\text{-}n\text{-}C_3H_7)_2$ (II). The procedure was identical with that described above. Chlorpropamide was used instead. Yield: 70%. Anal. Calcd for $C_{20}H_{24}N_4Cl_2O_6S_2Hg$ (M_r = 751.6): C, 31.93; H, 3.19; N, 7.45; Hg, 26.67. Found: C, 30.49; H, 3.18; N, 8.10; Hg, 25.94.

Potassium Tris[*N*-((propylamino)carbonyl)-4-chlorobenzenesulfonamido]cadmate, $K[Cd(ClC_6H_4SO_2NCONH\text{-}n\text{-}C_3H_7)_3]$ (III). To a 100 mL solution of 60 mmol of chlorpropamide and 60 mmol of KOH in absolute ethanol was added a suspension of 20 mmol of $Cd(CH_3COO)_2$ in 20 mL of absolute ethanol. The initially appearing white precipitate dissolved with stirring. When the mixture was stirred for ca. 3 h, a white microcrystalline product started to separate. The mixture of the reaction was reduced in volume and cooled to −10 °C. More white microcrystalline solid was deposited, which was collected by filtration, washed with ethanol and diethyl ether, and dried in vacuo. Recrystallized from CH_3CN/ether. Yield: ca. 60% based on metal. Anal. Calcd for $C_{30}H_{36}N_6KO_9S_3Cl_3CdK$ (M_r = 976.5): C, 36.86; H, 3.68; N, 8.60; Cd, 11.36; K, 3.99. Found: C, 36.60; H, 3.71; N, 8.43; Cd, 11.02; K, 3.80. X-ray powder pattern spacings (Å): 12.8 (vs), 9.25 (s), 7.75 (vw), 7.20 (m), 6.20 (s), 5.30 (w), 4.70 (s), 4.20 (vw), 4.10 (vw), 3.85 (m), 3.70 (vw), 3.55 (m), 3.35 (w), 3.25 (m), 3.05 (w).

Potassium Tris[*N*-((butylamino)carbonyl)-4-methylbenzenesulfonamido]cadmate, $K[Cd(CH_3C_6H_4SO_2NCONH\text{-}n\text{-}C_4H_9)_3]$ (IV). The procedure was identical with that described above. Tolbutamide was used instead. Yield: 75%. Anal. Calcd for $C_{36}H_{51}N_6O_9S_3CdK$ (M_r = 957): C, 45.14; H, 5.32; N, 8.77; Cd, 11.59; K, 4.07. Found: C, 44.98; H, 5.29; N, 8.89; Cd, 11.06; K, 3.98. X-ray powder pattern spacings (Å): 17.00 (s), 13.00 (vs), 10.90 (s), 9.00 (s), 8.00 (s), 7.60 (s), 7.00 (m), 6.40 (m), 5.90 (m), 5.20 (m), 4.70 (s), 4.50 (vw), 4.35 (w), 4.20 (vw), 4.00 (vw), 3.85 (m), 3.40 (s), 3.35 (m), 3.25 (m), 3.15 (m), 3.05 (w).

Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement Data for $Hg(CH_3C_6H_4SO_2NCONH\text{-}n\text{-}Bu)_2$ and $K[Cd(ClC_6H_4SO_2NCONH\text{-}n\text{-}Pr)_3]\cdot CH_3CN$

	$C_{24}H_{34}N_4O_6S_2Hg$	$C_{32}H_{39}N_7O_9Cl_3S_3KCd$
M_r	739.27	1019
a, Å	10.171 (4)	8.292 (2)
b, Å	9.901 (5)	15.407 (4)
c, Å	13.800 (7)	18.162 (5)
α, deg	90.00	71.08 (2)
β, deg	94.53 (3)	83.92 (2)
γ, deg	90.00	88.92 (2)
Z; *V*, Å^3	2; 1385 (1)	2; 2182 (1)
d_{calcd}, g/cm^3	1.78	1.55
d_{obsd},^{a} g/cm^3	1.80	1.56
space group	$P2_1/a$	$P\bar{1}$
cryst dimens, mm	0.20 × 0.21 × 0.02	0.30 × 0.20 × 0.05
abs coeff, cm^{-1}	56.88	9.30
radiation	Mo Kα_1 (0.709 26 Å)	Mo Kα_1 (0.709 26 Å)
no. of data collcd; range, deg	1524; $2\theta_{max}$ = 40	4476; $2\theta_{max}$ = 40
no. of unique data	1312	3627
no. of data used in refinement ($F_o^2 > 3\sigma(F_o^2)$)	881	3319
scan speed (min, max), deg/min	5.0; 29.2	4.0; 29.3
no. of atoms in the asym unit	71	92
no. of variables	169	265
phasing technique	direct methods	Patterson
R,^{b} %	4.06	5.81
R_w,^{c} %	3.89	5.96

^{a} Determined by flotation in a $CHBr_3$/pentane mixture. ^{b} $R = \sum|\Delta F|/\sum|F_o|$. ^{c} $R_w = [\sum w(\Delta F)^2/\sum w(F_o^2)]^{1/2}$.

Potassium Bis[*N*-((butylamino)carbonyl)-4-methylbenzenesulfonamido]argentate, $K[Ag(CH_3C_6H_4SO_2NCONH\text{-}n\text{-}C_4H_9)_2]$ (V). To a 60 mL solution of 40 mmol of tolbutamide and 40 mmol of KOH in ethanol was added a solution of 20 mmol of $AgNO_3$ in 50 mL of ethanol/water (80:20). When the mixture was stirred for ca. 30 min, a white microcrystalline product started to separate. The reaction mixture was reduced in volume to one-third of the original volume and cooled to 0 °C. The white microcrystalline solid that deposited was collected by filtration, washed with ethanol/water (80:20) and diethyl ether, and dried in vacuo. Yield: ca. 50% based on metal. Anal. Calcd for $C_{24}H_{34}N_4O_6S_2AgK$ (M_r = 584.86): C, 42.00; H, 4.96; N, 8.16; Ag, 15.77. Found: C, 41.21; H, 4.90; N, 8.09; Ag, 15.63.

Potassium Bis[*N*-((propylamino)carbonyl)-4-chlorobenzenesulfonamido]argentate, $K[Ag(ClC_6H_4SO_2NCONH\text{-}n\text{-}C_3H_7)_2]$ (VI). The procedure was identical with that described above. Chlorpropamide was used instead. Yield: 45%. Anal. Calcd for $C_{20}H_{24}N_4O_6S_2Cl_2AgK$ (M_r = 697.86): C, 34.39; H, 3.43; N, 8.02; Ag, 15.46. Found: C, 34.48; H, 3.26; N, 8.05; Ag, 15.39.

Crystallographic Studies

Collection of Data. Single crystals of I were obtained from slow cooling of an ethanolic solution to −10 °C. Crystals of III were obtained by the slow evaporation of a CH_3CN solution. Both crystals were white flat plates and were enclosed in glass capillaries. Due to severe solvent loss followed by crystal disintegration, crystals of III were enclosed with CH_3CN solvent. Details concerning crystal characteristics and X-ray diffraction methodology are shown in Table I. Intensity data were collected on a Nicolet P3/F four-circle diffractometer. A detailed description of the instrument and the data acquisition procedures have been described earlier.[6] The accurate cell dimensions for I and III were refined by using 20–25 machine-centered reflections with 2θ values between 20 and 40° (Mo Kα_1, λ = 0.709 26 Å). Intensity data were collected from one-fourth of the reciprocal lattice sphere for the monoclinic I ($h,\pm k,\pm l$) and from half of the sphere for the triclinic III, ($h,-k,\pm l$). The intensities of the three check reflections (004), (040), and

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Table II. Infrared[a] and Nuclear Magnetic Resonance (NMR) Spectra of Sulfonylurea–Metal Complexes

compd	IR,[d] cm^{-1}					NMR,[c] ppm						
									CH$_2$			
	ν(C–H)	ν(C$\overset{\dots}{-}$O)	ν(C$\overset{\dots}{-}$N)	ν_{as}(SO$_2$)	ν_s(SO$_2$)	aromatic	p-CH$_3$	NH	α	β	γ	CH$_3$
Hg(CH$_3$C$_6$H$_4$SO$_2$NCONHC$_4$H$_9$)$_2$	3360	1650	1523	1325	1159	7.84 (d)[b] 7.37 (d)	2.11 (s)	6.45 (s, br)	3.14 (m)	1.37 (m)	1.15 (m)	0.83 (t)
Hg(ClC$_6$H$_4$SO$_2$NCONHC$_3$H$_7$)$_2$	3389	1636	1532	1322	1151	7.89 (d) 7.50 (d)		6.69 (s, br)	2.86 (m)	1.29 (m)		0.73 (t)
K[Cd(CH$_3$C$_6$H$_4$SO$_2$NCONHC$_4$H$_9$)$_3$]	3358	1594	1544	1315	1165	7.71 (d) 7.18 (d)	2.31 (s)	6.36 (s, br)	2.89 (m)	1.24 (m)	1.14 (m)	0.78 (t)
K[Cd(ClC$_6$H$_4$SO$_2$NCONHC$_3$H$_7$)$_3$]	3375	1584	1541	1319	1169	7.81 (d) 7.43 (d)		6.36 (s, br)	2.84 (m)	1.31 (m)		0.73 (t)
K[Ag(CH$_3$C$_6$H$_4$SO$_2$NCONHC$_4$H$_9$)$_2$]	3383	1634	1520	1297	1150	7.72 (d) 7.21 (d)	2.32 (s)	6.44 (s, br)	2.88 (m)	1.28 (m)	1.15 (m)	0.79 (t)
K[Ag(ClC$_6$H$_4$SO$_2$NCONHC$_3$H$_7$)$_2$]	3382	1632	1515	1290	1150	7.80 (d) 7.43 (d)		6.35 (s, br)	2.86 (m)	1.28 (m)		0.72 (t)

[a] Selected frequencies. [b] Key: s = singlet; d = doublet; t = triplet; m = multiplet; br = broad. [c] At ambient temperature. [d] Labeling scheme:

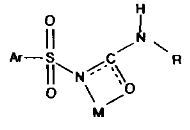


Table III. Fractional Atomic Coordinates for Hg(CH$_3$C$_6$H$_4$SO$_2$NCONH-n-Bu)$_2$

atom	x	y	z	U, Å
Hg	0.5000 (0)	0.5000 (0)	0.0000 (0)	0.04722
S	0.2002 (6)	0.4769 (7)	0.0370 (5)	0.0424
O(1)	0.1145 (14)	0.3619 (16)	0.0309 (11)	0.0496
O(2)	0.2192 (14)	0.5543 (15)	−0.0509 (11)	0.0526
O(3)	0.5030 (16)	0.3420 (17)	0.1858 (12)	0.0509
N(1)	0.3513 (17)	0.4307 (21)	0.0787 (13)	0.0410
N(2)	0.2875 (18)	0.2877 (18)	0.2006 (15)	0.0438
C(1)	0.1437 (22)	0.5856 (25)	0.1269 (16)	0.0393
C(2)	0.1919 (24)	0.7165 (27)	0.1345 (18)	0.0496
C(3)	0.1392 (28)	0.8040 (25)	0.2003 (20)	0.0601
C(4)	0.0449 (25)	0.7624 (27)	0.2582 (17)	0.0492
C(5)	0.0003 (23)	0.6337 (26)	0.2499 (18)	0.0514
C(6)	0.0476 (22)	0.5459 (20)	0.1828 (16)	0.0405
C(7)	−0.0131 (29)	0.8632 (27)	0.3269 (20)	0.0800
C(8)	0.3862 (27)	0.3484 (22)	0.1587 (16)	0.0373
C(9)	0.3157 (24)	0.2044 (22)	0.2845 (18)	0.0490
C(10)	0.3046 (45)	0.2672 (39)	0.3757 (27)	0.1838
C(11)	0.2017 (45)	0.3536 (49)	0.4107 (30)	0.1804
C(12)	0.1938 (47)	0.4094 (54)	0.4970 (31)	0.1590

(400) were monitored every 90 reflections. The data were collected by using the $\theta/2\theta$ scan technique.

Reduction of Data. The raw data were reduced to net intensities, estimated standard deviations were calculated on the basis of counting statistics, Lorentz–polarization corrections were applied, and equivalent reflections were averaged. The estimated standard deviation of the structure factor was taken as the larger of that derived from counting statistics and that derived from the scatter of multiple measurements.

The least-squares program used minimizes $\sum(w|\Delta F|)^2$. The weighting function used throughout the refinement of the structure gives zero weight to those reflections with $F^2 < 3\sigma(F^2)$ and $w = 1/\sigma^2(F^2)$ to all others $[\sigma^2(F^2) = (0.06F^2)^2 + \sigma^2(F^2)$ (from counting statistics)]. This program was part of the SHELX76 crystallographic package. Computations were carried out on an Amdahl 470/V6 computer. An analytical absorption correction was applied to the data of Hg(CH$_3$C$_6$H$_4$SO$_2$NCONH-n-Bu)$_2$. In view of the relatively small μ value (Table I) of the crystal of K[Cd(ClC$_6$H$_4$SO$_2$NCONH-n-Pr)$_3$] and on the basis of azimuthial scans of several reflections, no absorption correction was applied to the data of III.

Determination of the Structure of Hg(CH$_3$C$_6$H$_4$SO$_2$NCONH-n-Bu)$_2$ (I). The crystal structure was solved by the direct methods, routine SOLV of the SHELXTL package of crystallographic programs. The correct E map was calculated from starting phases obtained by placing the Hg atom at the 0.5, 0.5, 0.0 inversion center. (There are two molecules per unit cell, and therefore the Hg atom is required to reside at the crystallographic center of symmetry.) The positions of the S, O, and N atoms were determined this way. The rest of the non-hydrogen atoms were located subsequently from successive Fourier electron density difference maps, followed by full-matrix least-squares refinement. Isotropic refinement of the model gave a conventional R value of 0.105. At this point all atoms were assigned anisotropic temperature factors and the least-squares refinement continued. After four cycles the R value was 0.0520. In the final cycles of refinement the positions of 17 hydrogen atoms were calculated and included in the structure factor calculation but were not refined (C–H, 0.95 Å). They were assigned arbitrarily temperature factors of $U = 0.09$ Å^2. After four more cycles the structure converged to $R = 0.0406$ and weighted $R_w = 0.0389$.

Determination of the Structure of K[Cd(ClC$_6$H$_4$SO$_2$NCONH-n-Pr)$_3$] (III). The Cd atom was located from sharpened Patterson synthesis map, and its location was used for initial phasing in a subsequent Fourier electron density calculation. The latter revealed the locations of the sulfur and chlorine atoms. A least-squares refinement at this point yielded $R = 0.33$. The rest of the non-hydrogen atoms were found in subsequent Fourier maps followed by least-square refinement. Last, a cocrystallized CH$_3$CN molecule was found. After four cycles of least-squares full-matrix refinement the R value was 0.11. At this point the refinement proceeded with anisotropic temperature factors assigned on the heavy Cd, K, S, and Cl atoms with $R = 0.061$ after two cycles. The positions of the hydrogen atoms were calculated (C–H, 0.95 Å) and were included in the structure factor calculation but were not refined. Four more cycles of least-squares refinement converged the model to $R = 0.058$ and $R_w = 0.059$.

Crystallographic Results. The final atomic positional parameters of the non-hydrogen atoms in Hg(CH$_3$C$_6$H$_4$SO$_2$NCONHCH$_2$CH$_2$CH$_2$CH$_3$)$_2$ and K[Cd(ClC$_6$H$_4$SO$_2$NCONHCH$_2$CH$_2$CH$_3$)$_3$] with standard deviations derived from the inverse matrices of the least-squares refine-

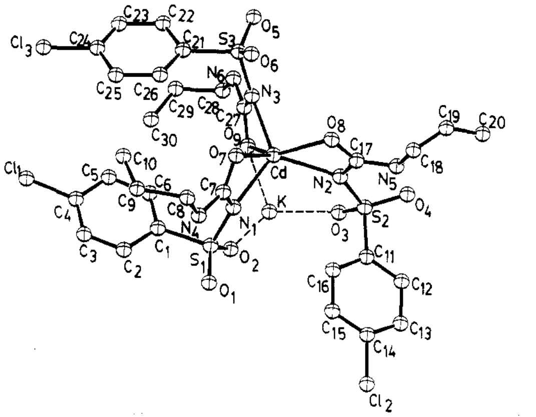


Figure 1. Structure of $K[Cd(ClC_6H_4SO_2NCONH\text{-}n\text{-}Pr)_3]$ with labeling scheme as drawn by ORTEP. The temperature factors were drawn isotropic for clarity.

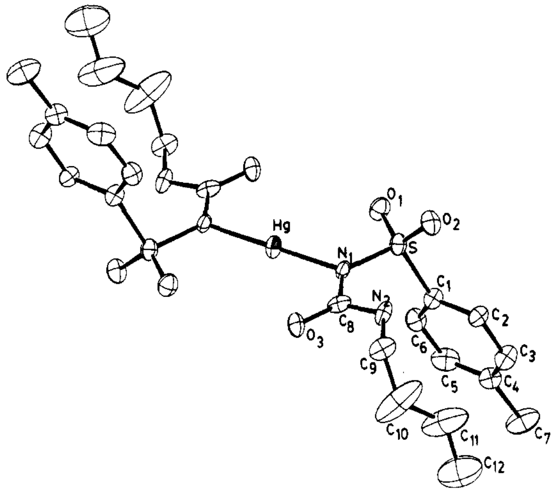


Figure 2. Structure of $Hg(CH_3C_6H_4SO_2NCONH\text{-}n\text{-}Bu)_2$ with labeling scheme as drawn by ORTEP.

ments are compiled in Tables III and IV, respectively. Intramolecular distances and angles for the anions in I and III are given in Tables V and VI. The structures and atom-labeling schemes are shown in Figures 1 and 2. A list of the final anisotropic temperature factors has been deposited as supplementary material.

Results and Discussion

Synthesis and Spectroscopy. The compounds reported here have been prepared in a way similar to that reported previously.[5] The reactions are simple and involve deprotonation of the ligand by KOH in ethanol followed by complexation with a metal salt.

$$RSO_2NHCONHR' + KOH \xrightarrow{EtOH} K^+[RSO_2NCONHR']^- + H_2O \quad (1)$$

$$Hg(CH_3COO)_2 + 2[RSO_2NCONHR']^- \rightarrow Hg(RSO_2NCONHR')_2 + 2CH_3COO^- \quad (2)$$

$$Cd(CH_3COO)_2 + 3K[RSO_2NCONHR'] \rightarrow K[Cd(RSO_2NCONHR')_3] + 2CH_3COOK \quad (3)$$

$$R = CH_3C_6H_4,\ ClC_6H_4;\ R' = n\text{-Bu},\ n\text{-Pr}$$

The Ag compound was prepared by using $AgNO_3$ as a starting material.

The compounds are white microcrystalline diamagnetic solids that appear to be air and moisture stable. They are soluble in Me_2SO, DMF, hot CH_3CN, and hot ethanol but are insoluble in benzene, toluene, CH_2Cl_2, and water.

These complexes exhibit characteristic IR spectra due to the ligand vibration modes. A compilation of the IR data is shown in Table II. The N–H stretch of the SO_2NHCO group, present in the spectra of the free ligands, is missing as expected upon coordination through that deprotonated nitrogen atom. The proton of this moiety is the most acidic and therefore the first to be deprotonated by base. The major characteristic of the IR spectra is the position of the C=O stretching vibration. The energy of this band depends upon the coordination mode of the sulfonylurea ligand. If the ligand is bound to the metal in a primarily monodentate fashion as is the case for Hg (vide infra), ν(CO) occurs at 1650 cm^{-1}. In the $Cd(L)_3$ complex the ν(CO) band occurs at a lower frequency, 1594 cm^{-1}, which indicates greater reduction of the C=O bond order, which in turn is a consequence of the bidentate mode of coordination. Clearly a decrease in the CO frequency is expected just by deprotonation of the free ligands. The extent of this decrease however should be equal in both complexes. Therefore any differences in the ν(CO) stretches between the Hg and Cd complexes should be primarily due to the differences in the mode of ligand coordination. In addition the

Table IV. Fractional Atomic Coordinates for $K[Cd(ClC_6H_4SO_2NCONH\text{-}n\text{-}Pr)_3]$

atom	x	y	z	U, Å^2
Cd	0.1164 (1)	0.4494 (1)	0.2061 (1)	0.0357
K	0.6001 (4)	0.4433 (2)	0.1859 (2)	0.0448
Cl(1)	0.8797 (11)	0.9337 (4)	0.2469 (4)	0.1655
Cl(2)	0.8092 (11)	0.0690 (5)	0.6096 (3)	0.1603
Cl(3)	1.2020 (12)	1.0019 (4)	0.0411 (6)	0.2106
S(1)	0.8912 (5)	0.5060 (3)	0.3577 (2)	0.0504
S(2)	0.9229 (4)	0.2331 (2)	0.2465 (2)	0.0431
S(3)	1.3006 (4)	0.6029 (2)	0.0347 (2)	0.0386
N(1)	1.0560 (13)	0.4835 (7)	0.3147 (6)	0.0139
N(2)	1.0752 (12)	0.2993 (7)	0.2266 (6)	0.0126
N(3)	1.1474 (12)	0.5464 (6)	0.0876 (5)	0.0108
N(4)	0.2325 (14)	0.5309 (8)	0.3905 (7)	0.0186
N(5)	1.2717 (17)	0.1820 (9)	0.2476 (8)	0.0240
N(6)	0.9559 (12)	0.6145 (7)	−0.0026 (6)	0.0123
O(1)	0.8927 (12)	0.4732 (7)	0.4417 (6)	0.0225
O(2)	0.7645 (12)	0.4731 (7)	0.3253 (6)	0.0205
O(3)	0.7861 (12)	0.2902 (7)	0.2246 (6)	0.0211
O(4)	0.9487 (12)	0.1587 (6)	0.2156 (5)	0.0195
O(5)	1.3051 (11)	0.6077 (6)	−0.0456 (5)	0.0185
O(6)	1.4380 (11)	0.5646 (6)	0.0763 (5)	0.0182
O(7)	1.3208 (11)	0.5070 (6)	0.2746 (5)	0.0179
O(8)	1.3349 (11)	0.3321 (6)	0.2206 (5)	0.0177
O(9)	0.8848 (10)	0.5276 (6)	0.1248 (5)	0.0146
C(1)	0.8794 (17)	0.6263 (9)	0.3282 (8)	0.0161
C(2)	0.8770 (19)	0.6738 (11)	0.3833 (10)	0.0227
C(3)	0.8738 (22)	0.7675 (13)	0.3562 (11)	0.0290
C(4)	0.8761 (23)	0.8168 (13)	0.2796 (11)	0.0284
C(5)	0.8792 (22)	0.7718 (12)	0.2247 (11)	0.0284
C(6)	0.8783 (19)	0.6761 (11)	0.2514 (9)	0.0229
C(7)	1.2076 (17)	0.5064 (9)	0.3260 (8)	0.0153
C(8)	0.3943 (20)	0.5570 (12)	0.4013 (10)	0.0263
C(9)	1.3957 (31)	0.6643 (16)	0.3926 (14)	0.0449
C(10)	1.3753 (34)	0.7253 (18)	0.3162 (15)	0.0539
C(11)	0.8963 (16)	0.1845 (9)	0.3497 (8)	0.0141
C(12)	0.9202 (19)	0.2365 (11)	0.3939 (9)	0.0221
C(13)	0.8902 (22)	0.2003 (13)	0.4776 (11)	0.0294
C(14)	0.8402 (24)	0.1125 (14)	0.5081 (11)	0.0315
C(15)	0.8149 (25)	0.0591 (15)	0.4684 (12)	0.0356
C(16)	0.8446 (21)	0.0953 (12)	0.3823 (10)	0.0265
C(17)	1.2312 (17)	0.2702 (9)	0.2319 (8)	0.0150
C(18)	1.4403 (30)	0.1509 (17)	0.2565 (15)	0.0444
C(19)	1.4991 (38)	0.1016 (21)	0.2166 (18)	0.0605
C(20)	1.4297 (33)	0.0299 (17)	0.2003 (15)	0.0523
C(21)	1.2748 (16)	0.7162 (9)	0.0367 (8)	0.0153
C(22)	1.2344 (18)	0.7859 (10)	−0.0309 (9)	0.0202
C(23)	1.2080 (22)	0.8747 (13)	−0.0283 (11)	0.0285
C(24)	1.2298 (24)	0.8923 (14)	0.0374 (12)	0.0325
C(25)	1.2685 (24)	0.8255 (14)	0.1057 (12)	0.0328
C(26)	1.2936 (19)	0.7361 (11)	0.1027 (9)	0.0215
C(27)	0.9901 (15)	0.5638 (8)	0.0688 (7)	0.0119
C(28)	0.7870 (16)	0.6387 (9)	−0.0224 (8)	0.0156
C(29)	0.7445 (20)	0.7360 (10)	−0.0268 (9)	0.0208
C(30)	0.7520 (22)	0.7546 (12)	0.0492 (10)	0.0276
NS	0.3454 (46)	0.1575 (27)	0.4970 (22)	0.0965
CS(1)	0.3898 (37)	0.2240 (22)	0.4537 (18)	0.0492
CS(2)	0.4745 (30)	0.3000 (17)	0.4048 (14)	0.0466

Table V. Interatomic Distances (Å) and Angles (deg) for Hg[p-MeC$_6$H$_4$SO$_2$NCONH-n-Bu]$_2$

Hg–N(1)	2.052 (17)	N(1)–S	1.66 (2)	S–C(1)	1.77 (2)
Hg–O(1)	2.941 (14)	N(1)–C(8)	1.40 (3)	C(1)–C(2)	1.40 (3)
Hg–O(2)	4.214 (14)	N(2)–C(8)	1.34 (3)	C(2)–C(3)	1.40 (3)
Hg–O(3)	3.004 (17)	C(8)–O(3)	1.22 (2)	C(3)–C(4)	1.36 (3)
Hg···S	3.146 (6)	N(2)–C(9)	1.43 (3)	C(4)–C(5)	1.36 (3)
S–O(1)	1.462 (15)	C(9)–C(10)	1.42 (4)	C(5)–C(6)	1.39 (3)
S–O(2)	1.434 (15)	C(10)–C(11)	1.46 (4)	C(6)–X(1)	1.35 (3)
mean	1.448	C(11)–C(12)	1.32 (5)	mean of six	1.38
C(4)–C(7)	1.53 (3)	mean C–C in n-Bu group	1.40		
Hg–N(1)–S	115 (1)	C(1)–C(2)–C(3)	119 (2)	N(1)–C(8)–O(3)	117 (2)
Hg–N(1)–C(8)	118 (2)	C(2)–C(3)–C(4)	121 (2)	N(2)–C(8)–O(3)	126 (2)
S–N(1)–C(8)	127 (2)	C(3)–C(4)–C(5)	119 (2)	N(1)–C(8)–N(2)	117 (2)
C(1)–S–O(1)	107 (1)	C(4)–C(5)–C(6)	121 (2)	C(8)–N(2)–C(9)	120 (2)
C(1)–S–O(2)	110 (1)	C(5)–C(6)–C(1)	120 (2)	C(10)–C(9)–N(2)	116 (2)
C(1)–S–N(2)	106 (1)	C(6)–C(1)–C(2)	120 (2)	C(9)–C(10)–C(11)	131 (4)
O(1)–S–O(2)	119 (1)	O(1)–Hg–N(1)	56.1 (6)	C(10)–C(11)–C(12)	130 (4)
O(2)–S–N(1)	105 (1)	O(3)–Hg–N(1)	48.0 (6)	C(3)–C(4)–C(7)	120 (2)
O(1)–S–N(1)	110 (1)	O(1)–Hg–O(3)	104.1 (4)	C(5)–C(4)–C(7)	122 (2)
S–C(1)–C(2)	119 (2)				
S–C(1)–C(6)	121 (2)				

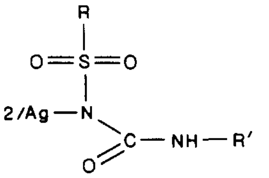
Table VI. Selected Interatomic Distances (Å) and Angles[a] (deg) for K[Cd(ClC$_6$H$_4$SO$_2$NCONH-n-Pr)$_3$]

Cd–N(1)	2.205 (10)	C(7)–O(7)	1.249 (15)	K–O(2)	3.163 (10)
Cd–N(2)	2.251 (10)	C(17)–O(8)	1.258 (14)	K–O(3)	2.713 (10)
Cd–N(3)	2.180 (10)	C(27)–O(9)	1.259 (13)	K–O(9)	2.684 (10)
mean[b]	2.212 (20)	mean	1.255 (15)	K–O(6)	2.693 (10)
Cd···K	3.989 (3)	N(1)–S(1)	1.586 (11)	K–O(7)	3.001 (10)
N(1)···O(7)	2.242 (14)	N(2)–S(2)	1.586 (11)	K–O(8)	2.724 (10)
N(2)···O(8)	2.212 (14)	N(3)–S(3)	1.603 (11)	mean	2.83 (8)
N(3)···O(9)	2.210 (13)	mean	1.592 (11)	mean S–C	1.764 (15)
mean	2.221 (14)	Cd–O(7)	2.544 (9)	mean Cl–C	1.721 (17)
C(7)–N(1)	1.371 (16)	Cd–O(8)	2.489 (9)	mean C–C[a,c]	1.38 (1)
C(17)–N(2)	1.358 (16)	Cd–O(9)	2.571 (8)	mean C–C[b,d]	1.45 (5)
C(27)–N(3)	1.379 (15)	mean	2.535 (24)	N(4)–C(8)	1.464 (19)
mean	1.369 (16)	S(1)–O(1)	1.445 (10)	N(5)–C(18)	1.472 (24)
C(7)–N(4)	1.379 (16)	S(1)–O(2)	1.438 (10)	N(6)–C(28)	1.488 (16)
C(17)–N(5)	1.334 (17)	S(2)–O(3)	1.422 (10)	mean	1.475 (20)
C(27)–N(6)	1.333 (15)	S(2)–O(4)	1.430 (10)		
mean	1.349 (17)	S(3)–O(5)	1.432 (10)		
mean of six	1.359 (17)	S(3)–O(6)	1.437 (10)		
		mean	1.434 (10)		
N(1)–Cd–O(7)	55.8 (3)	N(1)–Cd–N(2)	111.0 (4)	C(1)–S(1)–O(1)	107.5 (6)
N(2)–Cd–O(8)	55.3 (3)	N(1)–Cd–N(3)	126.4 (4)	C(1)–S(1)–O(2)	108.1 (6)
N(3)–Cd–O(9)	54.7 (3)	N(2)–Cd–N(3)	120.6 (3)	C(11)–S(2)–O(3)	106.5 (6)
mean	55.3 (3)	O(7)–Cd–O(8)	77.4 (2)	C(11)–S(2)–O(4)	107.0 (6)
O(7)–Cd–N(2)	122.9 (3)	O(7)–Cd–O(9)	133.1 (2)	C(21)–S(3)–O(5)	106.6 (6)
O(7)–Cd–N(3)	102.4 (3)	O(8)–Cd–O(9)	144.8 (2)	C(21)–S(3)–O(6)	107.7 (6)
O(8)–Cd–N(1)	111.6 (3)	N(1)–C(7)–O(7)	117.6 (1.2)	mean	107.2 (6)
O(8)–Cd–N(3)	108.8 (3)	N(2)–C(17)–O(8)	115.4 (1.2)	O(2)–K–O(3)	80.6 (3)
O(9)–Cd–N(1)	101.9 (3)	N(3)–C(27)–O(9)	113.7 (1.1)	O(2)–K–O(9)	73.0 (3)
O(9)–Cd–N(2)	103.2 (3)	N(1)–C(7)–N(4)	120.9 (1.2)	O(2)–K–O(6)	129.0 (3)
Cd–N(1)–C(7)	99.3 (8)	N(2)–C(17)–N(5)	122.3 (1.3)	O(2)–K–O(7)	77.6 (3)
Cd–N(2)–C(17)	98.7 (8)	N(3)–C(27)–N(6)	122.1 (1.1)	O(2)–K–O(8)	118.5 (3)
Cd–N(3)–C(27)	102.9 (7)	O(7)–C(7)–N(4)	121.5 (1.3)	O(3)–K–O(9)	83.5 (3)
Cd–O(7)–C(7)	87.2 (7)	O(8)–C(17)–N(5)	122.3 (1.3)	O(3)–K–O(6)	145.5 (3)
Cd–O(8)–C(17)	90.5 (7)	O(9)–C(27)–N(6)	124.2 (1.2)	O(3)–K–O(7)	132.0 (3)
Cd–O(9)–C(27)	88.3 (6)	C(7)–N(4)–C(8)	120.5 (1.2)	O(3)–K–O(8)	88.1 (3)
Cd–N(1)–S(1)	133.5 (6)	C(17)–N(5)–C(18)	121.7 (1.5)	O(9)–K–O(6)	92.4 (3)
Cd–N(2)–S(2)	136.2 (6)	C(27)–N(6)–C(28)	122.6 (1.1)	O(9)–K–O(7)	128.4 (3)
Cd–N(3)–S(3)	132.9 (6)	O(1)–S(1)–O(2)	117.6 (6)	O(9)–K–O(8)	164.5 (3)
N(1)–S(1)–C(1)	105.7 (6)	O(3)–S(2)–O(4)	117.3 (6)	O(6)–K–O(7)	74.5 (3)
N(2)–S(2)–C(11)	106.4 (6)	O(5)–S(3)–O(6)	118.3 (6)	O(6)–K–O(8)	87.7 (3)
N(3)–S(3)–C(21)	105.8 (6)			O(7)–K–O(8)	66.5 (3)
mean	106.0 (6)				

[a] The C–C–C angles in the aromatic rings range from 116.7 to 125.2 with a mean of 120°. The mean C–C–C angle in the n-propyl groups is 110° and ranges from 111 to 113°. [b] The standard deviation from the mean, σ, is reported: $\sigma = [\sum_{i=1}^{N} (X_i - \bar{X})^2/N(N-1)]^{1/2}$. [c] Within the phenyl ring. [d] Within the Pr chain.

$\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ stretching frequencies of the $\mathrm{SO_2N}\overset{\cdots}{-}\mathrm{C}$ fragment also follow a similar relationship. In the mercury compounds the bands occur at lower frequencies, 1523 and 1532 cm^{-1} for tolbutamide and chlorpropamide, respectively, compared with the corresponding ones in the Cd compounds (1544, 1541 cm^{-1}). By comparison the uncomplexed tolbutamide and chlorpropamide, show IR stretching vibrations at 1672 and 1563 cm^{-1} and 1660 and 1568 cm^{-1}, respectively, for C⋯O and C⋯N.[7] The stretching frequencies of the C⋯O bonds in the free drugs are higher than those in the complexes and typical of amido or ureido corresponding values.

These results suggest that the IR spectra of sulfonylurea–metal complexes may be used as diagnostic tools for the determination of the ligand coordination mode. The silver compounds show (C⋯O) and (C⋯N) vibrations at 1634 and 1632 cm^{-1} and 1520 and 1515 cm^{-1} for tolbutamide and chlorpropamide, respectively. A monodentate coordination is thereby proposed:

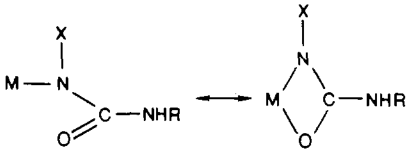


Finally the $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ stretching frequencies were observed in the 1280–1330-cm^{-1} and 1130–1170-cm^{-1} regions, respectively. The band positions did not change in comparison to those of the free ligand. This indicates that there is no interaction between the sulfonyl groups and the metal, which is also confirmed by the X-ray analysis (vide infra). Our results disagree with the original proposal that tolbutamide and chlorpropamide are bound to Hg and Cd via SO_2 oxygen atoms and carbonyl oxygen atoms.[5]

The ^{1}H NMR spectra (360 MHz) of these compounds were recorded in deuteriated Me_2SO. A compilation of ^{1}H NMR data is shown in Table II. The resonance lines of the aromatic ring protons lie between 7.10 and 7.84 ppm. The resonance lines of the N–H protons are found near 6.36–6.65 ppm and those of the aliphatic protons in the range from 0.73 to 3.14 ppm. The integrated proton ratios correspond to the proposed formulas.

Description of Structures. K[Cd($ClC_6H_4SO_2NCONH$-*n*-Pr)$_3$] (III). The structure comprises slightly interacting potassium cation atoms and tris[*N*-((propylamino)carbonyl)-4-chlorobenzenesulfonamido)]cadmate anions. The latter possesses neither crystallographic nor approximate symmetry. Figure 1 shows the K[CdL_3] ion pair with the labeling scheme. Selected interatomic distances and angles are found in Table VI.

The six-coordinate Cd atom assumes trigonal-prismatic geometry with two ketonic oxygen atoms, O(7) and O(8), and one imido nitrogen atom, N(3), occupying the corners of one trigonal face and two imido nitrogen atoms, N(1) and N(2), and the third ketonic atom, O(9), occupying the opposite trigonal face. The planes of the trigonal faces N(3)O(7)O(8) and N(1)N(2)O(9) are almost parallel with an angle of ~4°. The trigonal-prismatic coordination of the Cd atom is not especially surprising in view of the large ionic radius of this atom and the rather small bite of the ClC_6H_4NCONH-*n*-Pr ligand, 2.22 (1) Å. This arrangement is in agreement with Keppert's discussion about the relationship of the ionic radius, ligand bite, and coordination geometry of six-coordinate $M(AB)_3$ type complexes (AB, asymmetric bidentate ligand).[8] The Cd–N bonds range from 2.180 (10) to 2.251 (10) Å with an average of 2.212 (20) Å, and the Cd–O bonds range from 2.489 (9) to 2.571 (8) Å and average of 2.535 (24) Å, respectively. These are significantly longer than the ones found in the octahedral [Cd(acac)$_3$]$^-$ complex[9] by ~0.2 Å (2.300 Å). The relatively long Cd–O distances in conjunction with the "normal" Cd–N distance in II may imply that the coordination mode of the imido portion of the ligand is indeed a hybrid between monodentate and bidentate with the latter contribution being predominant. In a true bidentate coordination mode, shorter Cd–O distances would be expected.



It could be argued that coordination around the Cd atom occurs exclusively through the nitrogen atoms of the N⋯C⋯O bite of the sulfonylurea ligands to constitute a trigonal-planar environment. This is primarily due to the fact that the sum of the three N(*i*)–Cd–N(*j*) angles is 358°, very close to 360°. The positions of the oxygen atoms then would be a consequence of steric factors due to the trigonal-planar coordination. It appears, however, that such long Cd–O bonds are not uncommon in the literature. Cd–O bonds of a magnitude comparable to those reported here have been observed previously in a variety of compounds. In tris(pyridine)bis(*o*-hydroxybenzoato)cadmium(II) and bis(bis(*o*-hydroxybenzoato)cadmium(II)) dihydrate[10] the coordination geometry around the metal center is considered to be a pentagonal bipyramid with two bidentate *o*-hydroxybenzoate ligands. The latter are bound through their COO$^-$ groups with Cd–O bonds ranging from 2.375 (2) to 2.523 (2) Å. In Cd(NH_2CH_2COO)$_2H_2O$,[11] the coordination geometry about the Cd atom is described as octahedral with two coordinated H_2O molecules and a Cd–O distance of 2.50 Å. In addition, a distorted dodecahedron was ascribed to the coordination environment of the Cd atom in $Cd(NO_3)_2{\cdot}4H_2O$[12] with two bidentate nitrate groups. The Cd–O distances in these groups were found at 2.435 and 2.593 Å, well within the range found in the corresponding distances in (III). In view of these and numerous other instances of "long" Cd–O bonds, we prefer to describe the Cd coordination geometry in III as trigonal prismatic. To further assess this correlation of ligand-binding mode vs. metal type in group IIB (group 12[19]) (in view of this monodentate binding to mercury (vide infra)) the structure of the zinc analogue would be necessary.[13]

There appears to be a correlation between the Cd–N and Cd–O bonds within the same chlorpropamide ligand. The shortest Cd–N bond is associated with the longest Cd–O bond and vice versa. The possibility exists that the lengthening of the Cd–O bonds is due to the participation of the O(7), O(8), and O(9) atoms in the coordination sphere of the potassium counterion, thus sharing their electron density between two metal centers. Although this is quite likely, the clarification of this point must await a structural determination of the Cd(L_3)$^-$ anion in the presence of a large organic noninteracting cation (i.e., (R_4N)[Cd($ClC_6H_4SO_2NCONH$-*n*-Pr)$_3$]. The potassium and cadmium atoms alternate to form a zigzag chain approximately parallel to the *a* axis, with the potassium ion approaching the complex along the pseudo-3-fold axis so that O(2), O(3), and O(9) atoms participate in its coordination sphere. The rest of the three coordination sites are occupied by the O(8), O(7), and O(6) atoms of a neighboring Cd(L)$_3^-$ molecule. The six potassium oxygen bonds vary from 2.693 (10) to a long 3.163 (10) Å with a mean value of 2.83 Å. Although the angular geometry around the potassium ion is quite irregular, its approximate coordination sphere can be regarded as trigonal prismatic. K$^+$⋯Cd(L)$_3^-$ interactions have been previously observed

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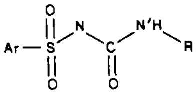
(13) We have prepared Zn(sulfonylurea)$_x^{n-}$ compounds in crystalline form. It appears that the stoichiometry of the complexes is directly dependent on the solvent medium and the Zn^{2+} source used. In methanol using zinc acetate as starting material, we have obtained mixed ligand complexes of the type Zn($ArSO_2NCONHR$)$_2$(CH_3COO)$_2^{2-}$. In CH_3CN using $ZnCl_2$, the Zn($ArSO_2NCONH$-R)$_n^-$ complexes appear to form. However, the C⋯N and C⋯O frequencies of these compounds (1544 and 1591 cm^{-1}, respectively, for tolbutamide) indicate a bidentate coordination of the sulfonylurea ligand similar to that of the cadmium compound. The results of this study will be reported in a forthcoming publication.

Table VII. Selected Interatomic Distances and Angles in Coordinated and Free Sulfonylureas[a]

	dist, Å				angles, deg				
	C–O	N–C	C–N′	N–S	N–C–N′	N–C–O	N′–C–O	C–N′–R	ref
$CH_3C_6H_4SO_2NHCONH$-*n*-Bu	1.11 (5)	1.52 (4)	1.38 (4)	1.73 (2)	102 (3)	125 (3)	132 (3)	110 (2)	18
$CH_3C_6H_4SO_2NCONH$-*n*-Bu[b]	1.22 (2)	1.40 (3)	1.34 (3)	1.66 (2)	117 (2)	117 (2)	126 (2)	120 (2)	this work
$ClC_6H_4SO_2NCONH$-*n*-Pr[c]	1.255 (15)	1.37 (2)	1.35 (2)	1.59 (1)	121 (2)	116 (2)	123 (2)	122 (2)	this work

[a] Labeling scheme for this table: 

. [b] Complexed with Hg^{2+}. [c] Complexed with Cd^{2+}.

in the structure of $K[Cd(acac)_3]\cdot H_2O$.[9] In the latter, five oxygen atoms of the acetylacetonate ligands interact with the potassium atom. The sixth site, in the approximate trigonal-prismatic arrangement around the alkali ion, is occupied by a H_2O molecule of solvation.

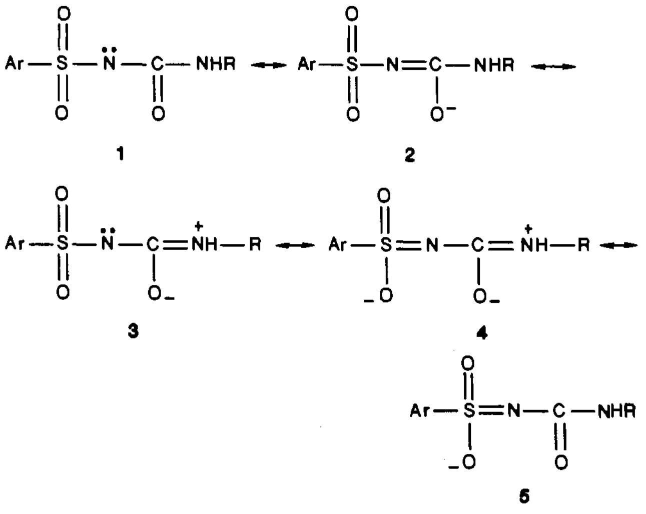
$Hg(CH_3C_6H_4SO_2NCONH$-*n*-Bu$)_2$ (I). The structure of (I) with the labeling scheme is shown in Figure 2 and consists of well separated neutral centro-symmetric molecules. Interatomic distances and angles are found in Table V. The coordination environment of the mercury atom, which lies at the ($^1/_2$, $^1/_2$, 0) center of symmetry, is linear. The tolbutamide ligand is bonded to the metal atom through the nitrogen N(1) atom which is located between the SO_2 and CO groups. The other imido N(2) nitrogen is protonated and bound to the terminal *n*-butyl group. The N(1)–Hg–N(1)′ angle is exactly 180° as required crystallographically. The Hg–N(1) distance is 2.052 (17) Å and compares with the values of 2.08 (3) and 2.06 (3) Å of other compounds containing a covalent Hg–N bond such as $(PhSO_2NAr)HgPh$.[14] The closest structural analogue of I is the long known mercury bis(acetamidate), which is also planar with collinear Hg–N bonds at 2.06 Å. The acetamide ligand in the latter is bound to the mercury atom in a monodentate fashion through its deprotonated N atom.

Apart from the obvious linear arrangement of nitrogen atoms, covalently bonded to the mercury atom via an apparent sp hybridization, there also exist some relatively short intramolecular contacts between the oxygen atoms of the SO_2 and CO functionalities, respectively. The shortest of them is the Hg⋯O(1) distance of 2.941 (14) Å. One more distance in I, Hg⋯O(3) at 3.004 (17) Å, is slightly longer than Hg⋯O(1) by 0.06 Å and is approximately equal to the van der Waals radius sum. These distances are unlikely to represent any significant bonding interaction. Intramolecular interactions of this sort have been previously observed in other mercury HgL_2 linear type compounds and their assessment as true bonding contacts has been ambiguous.[14] Several derivatives of (phenylmercury)benzenesulfonanilide ($PhHg(ArSO_2NAr')$, for instance) exhibit similar Hg⋯O distances.[14] The latter were characterized as significant. Recently the structure of the organomercury compound bis[2-(dimethylamino)methylphenyl]mercury(II) was reported and a similar short intramolecular Hg–N distance (2.89 Å) was described as definitely bonding.[17] Whether this close proximity represents any significant bonding interaction between those atoms is not clear, and it is still the subject of considerable discussion.[15,16] The value of the Hg⋯O(1) distance in I is smaller than the sum of the van der Waals radii of these atoms by ~0.1 Å. This however does not constitute a marked shortening, and it is our contention that this is most likely a crystal-packing effect and does not represent any significant interaction.

As in other HgL_2 type molecules, the mercury atom in I is regarded as primarily sp hybridized. Whether the p_x or p_y orbitals may engage in weak bonding interactions with the oxygen atoms of the SO_2 and CO groups remains to be established.

Structure of *p*-$XC_6H_4SO_2NCONHR$ Ligands (X = Cl, R = *n*-Pr; X = CH_3, R = *n*-Bu). Complexes I and III are the first examples of structurally characterized compounds containing sulfonylureas as ligands. The crystal structure of tolbutamide has been reported in its protonated form.[18] It will be compared with the corresponding complexed deprotonated form in I. It is clear from Figures 1 and 2 that the sulfonylurea derivatives can occur in two different coordination modes depending upon the nature of the metal atom. These binding modes are consistent with the tendencies of the metals studied, Hg and Cd, to form linear and six-coordinate complexes, respectively.

The structural portion of the sulfonylurea ligand important to this discussion is the NCONH "urea" moiety. The geometric features of the coordinated and free ligands are shown in Table VII. Upon deprotonation of the sulfonyl-bonded nitrogen atom, delocalization of the negative charge on the carbonyl double bond results by way of at least five possible resonance forms:



The structural parameters of Table VII suggest that resonance forms 1 and 2 are the predominant ones in the complexed ligands, although there are indications that contributions from resonance form 3 might be significant. The latter is corroborated from the near exact planarity of the

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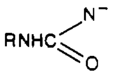
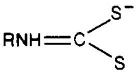


portions of the tolbutamide and chlorpropamide ligands in I and III and the relatively short HN–C distances at 1.35 (2) Å (Table VII). In addition the R–NH–C angles in both complexes are nearly 120° (Table VII) suggesting sp^2 hybridization around the NHR nitrogen. The contribuiton of resonance form 3 is reminiscent of the



form in dithiocarbamate complexes, which is responsible for the ability of the latter to stabilize high oxidation states in certain metals. By analogy the sulfonylurea ligands might possess similar coordination properties and be capable of supporting certain high oxidation states. This aspect of the coordination chemistry of sulfonylurea drugs is also being pursued in our laboratories.

Acknowledgment. We are indebted to Professor D. Coucouvanis for use of his X-ray diffraction equipment in the course of this study. We also thank Danae Christodoulou for assistance.

Supplementary Material Available: Tables of final atomic and thermal parameters for $Hg(CH_3C_6H_4SO_2NCONH\text{-}n\text{-}Bu)_2$ and $K[Cd(ClC_6H_4SO_2NCONH\text{-}n\text{-}Pr)_3]$ and a stereoview and a drawing of $K[Cd(ClC_6H_4SO_2NCONH\text{-}n\text{-}Pr)_3]$ with anisotropic temperature factors shown (5 pages); tables of structure factors ($10|F_o|/F_c$) (18 pages). Ordering information is given on any current masthead page.

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Mössbauer and EPR Spectroscopy of Catechol 1,2-Dioxygenase

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Mössbauer and EPR studies of catechol 1,2-dioxygenase from *Pseudomonas putida* and several of its complexes show that the iron center is high-spin ferric in character in all these complexes, including the enzyme–catechol complex and the steady-state intermediate obtained from the reaction of the enzyme, pyrogallol, and O_2. The Mössbauer spectrum of the native enzyme consists of two major components whose relative amounts vary with pH and buffer. One component exhibits a spectrum virtually identical with those of protocatechuate 3,4-dioxygenases from *Pseudomonas aeruginosa* and *Brevibacterium fuscum* with a common magnetic hyperfine constant, $A/g_n\beta_n$, of −21.0 T. This A value appears to be characteristic of this class of dioxygenases. It is closely matched by that of Fe(salen)benzoate (−20.9 T), a synthetic complex that approximates the coordination environment of the metal site. The binding of substrate and inhibitors alters the observed magnetic hyperfine parameters and zero-field splittings. $A/g_n\beta_n$ changes for −20.8 T for the phenol complex to −20.0 T for the thiophenol complex, indicating the greater covalency of the Fe–S bond. More interestingly, $A/g_n\beta_n$ for the catechol complex, −18.9 T, is the smallest in magnitude observed for a dioxygenase complex and indicates a greater delocalization of unpaired spin density away from the ferric center than in the phenol and thiophenol complexes. The unpaired spin density is presumably transferred onto the catechol, and this may enhance the reactivity of the substrate with dioxygen.

Introduction

Catechol 1,2-dioxygenase (catechol:oxygen 1,2-oxidoreductase (decyclizing); EC 1.13.11.1; CTD) from *Pseudomonas putida* is a non-heme iron enzyme that catalyzes the oxidative cleavage of catechols to *cis,cis*-muconic acids with the incorporation of the elements of dioxygen into the carboxylate functions of the product.[2] The enzyme has a molecular mass of 63 000 and consists of two nonidentical subunits of mass 30 000 and 32 000 and one iron.[3] It exhibits a visible absorption spectrum with an absorbance maximum near 460 nm ($\epsilon \sim 3500\ M^{-1}\ cm^{-1}$), which arises from tyrosinate-to-Fe(III) charge-transfer transitions.[4,5] CTD belongs to an emerging class of proteins exhibiting metal phenolate coordination, which also includes the transferrins, the purple acid phosphatases, and protocatechuate 3,4-dioxygenase (PCD).[6]

PCD catalyzes a reaction similar to that of CTD. Mössbauer studies of PCD (from *Pseudomonas aeruginosa* and *Brevibacterium fuscum*), its enzyme–substrate complex, and a steady-state intermediate generated upon oxygenation have shown that the active site iron remains high-spin ferric in these three forms.[7,8] These observations plus the persistence of the phenolate-to-Fe(III) charge-transfer band in transient intermediates[9,10] suggest that the charge and spin state of the iron are unchanged throughout the catalytic cycle. Thus a novel oxygenase mechanism in which the iron serves to activate substrate rather than O_2 has been proposed for these dioxygenases.[11] We report here a Mössbauer and EPR study of catechol 1,2-dioxygenase and several of its complexes, which shows that the iron center is high-spin ferric in these complexes, corroborating the earlier PCD studies.[7,8]

Data are also presented for the synthetic complex, Fe(salen)-BzO,[12] which exhibits Mössbauer parameters quite similar to those

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