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 (14) Abbreviations: en, ethylenediamine; dien, 1,4,7-triazheptane; trien, 1,4,7,10-tetraazadecane; tetren, 1,4,7,10,13-pentaaazatridecane; penten, *N,N,N',N'*-tetrakis(2-aminoethyl)ethylenediamine.
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Synthesis, Properties, and Structure of Iodosulfinate Salts

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A series of iodosulfinate salts, $[X](\text{ISO}_2^-)$ where X is a large organo cation, have been synthesized and characterized by vapor pressure tensimetric and spectroscopic methods. The compounds have SO_2 dissociation pressures of 0.5–17 Torr at ambient temperature and dissociation enthalpies of 5–19 kcal/mol. An x-ray diffraction study of $[\text{PPh}_3\text{Bz}](\text{ISO}_2^-)$ reveals a pyramidal ISO_2^- anion with an I–S distance of 3.251 (3) Å and I–S–O angles of 102.1 (5) and 105.7 (4)°. Crystallographic data: space group $\text{P}2_1/c$, $Z = 4$, $a = 10.92$ (1) Å, $b = 17.643$ (9) Å, $c = 15.49$ (2) Å, $\beta = 125.88$ (7)°, $R = 0.054$ for 2079 diffractometric reflections with $I \geq 2\sigma(I)$.

Introduction

The halosulfinate anions, XSO_2^- , which form by the Lewis acid–base interaction of SO_2 and halide ions, are well-known moieties which contain reversibly bound sulfur dioxide.¹ In recent years, these anions have received some spectroscopic and thermodynamic study, particularly in solution.^{2–8} Unfortunately, the variety of experimental conditions used in these studies makes quantitative evaluation of the actual complex strengths difficult. For example, it appears that the stability order of XSO_2^- in solution is often $\text{I} < \text{Br} < \text{Cl} < \text{F}$, but the order may be altered by solvent changes.^{6–8} The FSO_2^- anion is the most stable halosulfinate in the solid state.^{9,10} An approximate force constant treatment gave the S–X bond strength order as $\text{F} > \text{Cl} < \text{Br} < \text{I}$, consistent with observed shifts in electronic spectra of XSO_2^- species.⁸ An additional complication in earlier studies is the tendency for salts containing simple cations (such as alkali and alkaline earth metal ions) to be hygroscopic and to form highly solvated entities, e.g., $\text{KI} \cdot 4\text{SO}_2$.⁷

Although force constant calculations have been carried out on the FSO_2^- and ISO_2^- anions using assumed structural parameters, a structure determination has never been carried out for a simple halosulfinate ion.^{8,10} The only directly relevant structures are for $\text{Pt}(\text{PPh}_3)_2(\text{CH}_3)\text{I} \cdot \text{SO}_2$ ¹¹ and $\text{Cu}_2(\text{PPh}_2\text{Me})_4\text{I}_2 \cdot \text{SO}_2$ ¹² which contain SO_2 groups attached very weakly (I–S = 3.39–3.41 Å) to coordinated iodides.

During our study of substrates which bind SO_2 reversibly^{12,13} and as part of a more comprehensive study of SO_2 coordination chemistry in general,^{14–16} we discovered that large organo cations (such as $[\text{PPh}_3\text{Bz}]^+$ and $[\text{K}(\text{18-crown-6})]^+$) afford easily handled, crystalline, 1:1 ISO_2^- complexes. We decided to use the series to define more carefully certain physical properties of the ISO_2^- anion. We report herein the syntheses and physical properties of a series of ISO_2^- salts and an x-ray structure determination of a typical member of the series, $[\text{PPh}_3\text{Bz}](\text{ISO}_2^-)$.

Experimental Section

Materials, Equipment, and Experimental Methods. Reagent grade solvents and chemicals were used without further purification. The sulfur dioxide used was 99.98% pure (Matheson). Phosphonium and arsonium salts were purchased from Strem Chemical and Pressure

Chemical Co. and the crown ethers were purchased from Aldrich Chemical Co. Elemental analyses were performed by Galbraith Laboratories, Inc. Infrared and Raman spectra were recorded on Perkin-Elmer 521 and Cary 82 spectrometers, respectively.

Measurements of SO_2 Dissociation Pressures and Stoichiometries. To determine relative stabilities and stoichiometries of the various SO_2 adducts, the solid complex was placed in a glass tube which was then attached via an O-ring joint to a grease-free tensimeter or to a small evacuable manifold connected to a Validyne Engineering Corp. AP10 absolute pressure transducer (0–100 Torr). After careful pumping of the system at -63°C , the dissociation pressure of the sample was monitored as a function of temperature and time. Similarly, SO_2 :I ratios were determined by complete decomplexation of SO_2 at 70–120 °C and measurement of the SO_2 evolved using a calibrated portion of the vacuum system.

Preparation of the Iodosulfinate Compounds. The general procedure involved bubbling SO_2 through a warm solution of the appropriate iodide salt in acetonitrile solution, followed by addition of diethyl ether. Since the preparations differed only in detail, we present only representative preparations for salts containing phosphonium and crown ether complexed metal cations. The selenocyanate- and thiocyanate- SO_2 compounds were prepared similarly. Characterization data for the complexes are presented in Tables I and II.

$[\text{PPh}_3\text{Bz}](\text{ISO}_2^-)$. Sulfur dioxide was bubbled through a warm solution of triphenylbenzylphosphonium iodide (1.00 g, 2.08 mmol) in 5 mL of warm acetonitrile, giving a bright orange-yellow solution. Diethyl ether (20 mL) saturated with sulfur dioxide was added dropwise and the resulting mixture was allowed to stand for 2 h at 0 °C. The bright yellow crystals which formed were collected on a frit, washed twice with 5-mL portions of SO_2 -saturated diethyl ether, and dried under a stream of SO_2 . Yield 1.05 g (93%).

$[\text{Rb}(\text{18-crown-6})](\text{ISO}_2^-)$. Rubidium iodide (2.12 g, 10 mmol) and 18-crown-6 (2.64 g, 10 mmol) were dissolved in 200 mL of warm acetonitrile. Sulfur dioxide was bubbled through the solution for several minutes and the volume of the resulting orange solution was reduced to 20 mL using a hot plate. Upon addition of 10 mL of SO_2 -saturated diethyl ether, an orange crystalline product precipitated. The product was collected on a frit, washed twice with 10-mL portions of SO_2 -saturated diethyl ether, and dried under a stream of SO_2 . Yield 2.8 g (51%).

Collection and Reduction of the Crystallographic Data, Structure Solution, and Refinement for $[\text{PPh}_3\text{Bz}](\text{ISO}_2^-)$. Unless otherwise noted, crystallographic procedures were as described in earlier publications from this laboratory.^{15,17} Details of the data collection are given in Table III. A crystal was selected from the preparative batch described above and encased in a thin veneer of epoxy cement to inhibit loss

Table I. Characterization Data for the X-SO₂ Complexes

Compd	% C		% H		% S		% other		Mp, ^a °C	% yield
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found		
[K(18-crown-6)](ISO ₂)	29.15	29.00	4.89	5.85			25.67 (I)	24.10	246-248	71
[Rb(18-crown-6)](ISO ₂)	26.65	26.35	4.47	6.16			23.47 (I)	22.15	220-223	51
[AsPh ₄](ISO ₂)	50.19	51.59	3.51	3.42	6.06	5.58	22.09 (I)	23.91	309-312	70
[PPh ₃ Bz](ISO ₂)	55.16	56.22	4.07	3.59					265-267	93
[Ph ₃ P-N-PPh ₃](ISO ₂)	59.27	58.42	4.15	4.11	4.39	4.25	17.39 (I)	17.33	239-242	88
[Na(18-crown-6)](NCSO ₂)	38.13	37.78	5.91	6.05	15.66	15.55	3.42 (N)	2.69	138-139	82
[K(18-crown-6)](NCSeSO ₂)	33.05	32.49	5.12	5.47	6.79	6.46	2.96 (N)	2.48	185-187	80
[K(18-crown-6)]I ₃	21.07	22.34	3.54	3.81	0.00 ^b	0.01 ^b	55.65 (I)	55.56	206-208 dec	16

^a Melting points were taken in open capillaries at heating rates of ~10 °C min⁻¹. In most instances nearly complete decolorization of the compound occurred well before the melting point was reached. Hence the quoted values actually represent the melting of the uncomplexed salt. ^b % Se.

Table II. Tensimetric and Infrared Data for the X-SO₂ Complexes

Compd	Mol of SO ₂ /mol of complex	P _{diss} at 295 K, Torr	ΔH, ^f kcal/mol	SO ₂ vibrations, ^a cm ⁻¹		
				ν _{as} (SO)	ν _s (SO)	δ(SO ₂)
[K(18-crown-6)](ISO ₂)	0.98	0.5	14.7	<i>b</i>	<i>b</i>	530
[Rb(18-crown-6)](ISO ₂)	1.03	11.4	9.1	1289	1098	531
[AsPh ₄](ISO ₂)	0.95	0.6	19.1	1264	1095	518
[PPh ₃ Bz](ISO ₂)	0.98	9.2	13.7	1300	1123	514, 524
[Ph ₃ P-N-PPh ₃](ISO ₂)	1.03	13.2	5.7	1277	1093	523
[Na(18-crown-6)](NCSO ₂) ^d	1.02	5.3	<i>c</i>	<i>b</i>	1117	498, 506
[K(18-crown-6)](NCSeSO ₂) ^e	1.08	17.3	<i>c</i>	<i>b</i>	1102	525

^a Infrared spectra taken as Nujol mulls. Raman spectra were taken on powdered samples in glass capillaries. ^b SO₂ absorptions obscured by other bands. ^c Compound decomposed at elevated temperatures. ^d ν_{CN} = 2095, 2067, 2040 (w), 1983 (w); ν_{CS} = 748; δ_{NCS} = 469 cm⁻¹. For the compound [Na(18-crown-6)](NCS): ν_{CN} = 2067, 2041; ν_{CS} = 751; δ_{NCS} = 469 cm⁻¹. For K[NCS]: ν_{CN} = 2053; ν_{CS} = 748; ν_{NCS} = 486, 471 cm⁻¹. ^e ν_{CN} = 2093, 2065; ν_{CSe} = 546 (sh); δ_{NCSe} = 403 cm⁻¹. For the compound [K(18-crown-6)](NCSe), ν_{CN} = 2063; ν_{CSe} = 531; δ_{NCSe} = 408 cm⁻¹. For K[NCSe]: ν_{CN} = 2070; ν_{CSe} = 558; δ_{NCSe} = 404, 416 cm⁻¹. ^f Dissociation enthalpies were determined from the slope of the plot of ln P_{SO₂} vs. 1/T.

of SO₂. The intensity of a standard reflection declined by approximately 10% during data collection due to crystal decomposition, and an appropriate rescaling correlation was applied by interpolation between adjacent standards. The structure was solved and refined in a straightforward manner by the heavy-atom method. Hydrogen atoms were included (but not refined) in idealized positions^{12,18} with isotropic thermal parameters of 5.0 Å². Final atomic parameters are given in Table IV and selected interatomic distances and angles are presented in Table V. Structure factors are available as supplementary material.

Discussion

The iodosulfinate salts reported herein are formed conveniently and in good yield by precipitation from SO₂-saturated acetonitrile solutions of the appropriate iodide salts. The yellow to orange complexes seem stable indefinitely when stored under a partial pressure of SO₂, but noticeably decolorize over a period of hours when a partial pressure of SO₂ is not present. The compounds are well-defined, generally nonhygroscopic crystalline substances which are easy to handle in air for short periods of time without significant decomposition. These properties are in contrast to the properties of halosulfinate salts containing small counterions such as Na⁺.

By similar methods, the complexes [Na(18-crown-6)](NCS·SO₂) and [K(18-crown-6)](NCSe·SO₂) were prepared. These substances have physical properties similar to those of the iodosulfinate salts and apparently are the first isolated selenocyanate- and thiocyanate-SO₂ complexes to be reported. Our procedures failed to give well-defined, isolable SO₂ adducts with other halides (F⁻, Cl⁻, Br⁻) and pseudohalides (SeO₃²⁻, N₃⁻, NCO⁻, ClO₃⁻, BrO₃⁻, SO₃⁻, CN⁻). However, in many cases color changes indicative of complexation were observed, and adducts have been reported previously with a few of these anions. Redox reactions occurred with S²⁻, SH⁻, and SR⁻. A tensimetric experiment with [Co(en)₃]I₃ and liquid SO₂ gave a weak complex (SO₂ pressure > 200 Torr at 22 °C) with formulation [Co(en)₃]I₃·2SO₂ and reaction of SO₂ with [Me₃NPh]₂[CoI₄] gave a mixture of CoI₂ and [Me₃NPh]I.

Table III. X-Ray Data Collection Description

Empirical formula	ISO ₂ PC ₂₅ H ₂₂	No. of unique reflections collected	3180
Formula wt	544.4	No. of reflections with I ≥ 2σ(I)	2079
Systematic absences	0k0 (k = 2n + 1), h0l (h = 2n + 1)	Crystal dimensions, mm	0.12 × 0.12 × 0.24
Laue symmetry	2/m	Crystal faces	{010}; {100}; two faces approximated as (5, 1, 12) and (5, 1, 12)
Space group	P2 ₁ /c	μ, cm ⁻¹	15.1
ρ _{obsd} , g/cm ³ (by flotation in CH ₃ I/C ₆ H ₆)	1.46	Transmission coefficients (min, max)	0.84-0.85
ρ _{calcd} , g/cm ³	1.495	Cell parameter refinement data	12 reflections with 40 < 2θ < 44°
a, Å	10.92 (1)	Diffraction method	Computer-controlled Picker FACS-1
b, Å	17.643 (9)	Takeoff angle, deg	3.0
c, Å	15.49 (2)	Temp, °C	22 ± 3
β, deg	125.88 (7)	Final R	0.054
λ, Å	0.70930	Final R _w	0.037
Z	4		
Scan method	θ-2θ step scan		
Base scan width, deg	2.0		
Step width, deg	0.05		
θ _{min} , θ _{max} , deg	5, 45		

Addition of SeO₂ to a solution containing 18-crown-6 and KI did not lead to an isolable ISeO₂⁻ anion, but after several days the triiodide salt [K(18-crown-6)]I₃ precipitated. In an earlier study, solutions containing ISeO₂⁻ were studied spectroscopically, but the ISeO₂⁻ anion was identified immediately after mixing the components.³

The elemental analyses (Table I) and SO₂:complex ratios (Table II) show that in each complex the SO₂:I (or SO₂:NCS or SO₂:NCSe) ratio is 1:1. When heated at a rate of 10 °C min⁻¹, all of the compounds release SO₂ rapidly, usually are

Table IV. Final Least-Squares Parameters

A. Positional and Isotropic Thermal Parameters ^a									
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
I	-0.17929 (7)	-0.13777 (3)	0.12034 (5)	<i>b</i>	C11	0.270 (1)	0.1604 (5)	0.2328 (7)	5.3 (2)
S	0.1389 (4)	-0.0584 (2)	0.3052 (3)	<i>b</i>	C12	0.3421 (9)	0.1161 (4)	0.1991 (6)	4.4 (2)
O1	0.2472 (9)	-0.1010 (5)	0.3135 (7)	<i>b</i>	C13	0.6672 (8)	-0.0570 (4)	0.3277 (5)	2.7 (2)
O2	0.136 (1)	-0.0628 (9)	0.3908 (8)	<i>b</i>	C14	0.8224 (9)	-0.0590 (4)	0.3929 (6)	3.7 (2)
P	0.5681 (2)	0.0200 (1)	0.2365 (2)	<i>b</i>	C15	0.8937 (9)	-0.1199 (5)	0.4650 (6)	4.4 (2)
C1	0.6974 (8)	0.0867 (4)	0.2428 (6)	2.7 (2)	C16	0.8113 (9)	-0.1755 (5)	0.4740 (6)	4.2 (2)
C2	0.7912 (9)	0.0633 (3)	0.2146 (6)	3.4 (2)	C17	0.6567 (9)	-0.1738 (4)	0.4047 (6)	3.7 (2)
C3	0.8850 (9)	0.1154 (4)	0.2123 (6)	4.1 (2)	C18	0.5816 (9)	-0.1139 (4)	0.3322 (6)	3.7 (2)
C4	0.8831 (9)	0.1902 (5)	0.2381 (6)	4.3 (2)	C19	0.4562 (8)	-0.0143 (4)	0.1003 (6)	3.1 (2)
C5	0.791 (1)	0.2139 (5)	0.2625 (7)	4.5 (2)	C20	0.3524 (8)	-0.0805 (4)	0.0744 (6)	3.0 (2)
C6	0.6958 (9)	0.1636 (4)	0.2668 (6)	3.9 (2)	C21	0.3928 (8)	-0.1521 (5)	0.0650 (6)	4.0 (2)
C7	0.4580 (8)	0.0671 (4)	0.2711 (6)	2.7 (2)	C22	0.295 (1)	-0.2133 (5)	0.0354 (7)	5.3 (2)
C8	0.5021 (9)	0.0615 (5)	0.3750 (6)	4.0 (2)	C23	0.159 (1)	-0.2014 (5)	0.0177 (7)	5.7 (2)
C9	0.426 (1)	0.1066 (5)	0.4056 (7)	5.1 (2)	C24	0.1169 (9)	-0.1326 (6)	0.0279 (7)	5.2 (2)
C10	0.312 (1)	0.1542 (5)	0.3339 (7)	4.8 (2)	C25	0.212 (1)	-0.0688 (5)	0.0562 (6)	4.5 (2)

B. Anisotropic Thermal Parameters						
	β_{11}	β_{22}	β_{33}	$2\beta_{12}$	$2\beta_{13}$	$2\beta_{23}$
I	0.0154 (1)	0.00260 (2)	0.00760 (5)	0.0030 (1)	0.0123 (1)	0.00004 (8)
S	0.0175 (6)	0.0081 (2)	0.0150 (4)	0.0010 (6)	0.0118 (9)	-0.0070 (5)
O1	0.022 (2)	0.0114 (6)	0.022 (1)	-0.001 (2)	0.024 (2)	-0.013 (1)
O2	0.021 (2)	0.033 (1)	0.013 (1)	-0.014 (2)	0.014 (2)	-0.012 (2)
P	0.0100 (3)	0.00231 (9)	0.0040 (2)	0.0008 (3)	0.0077 (4)	0.0002 (2)

^a Throughout this paper, standard deviations for the least significant digit are given in parentheses. ^b Refined anisotropically. The anisotropic thermal parameters are defined by the expression $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Table V. Selected Interatomic Distances (Å) and Angles (deg)^a

I-S	3.251 (3)	P-C1	1.796 (7)
S-O1	1.342 (8)	P-C7	1.783 (7)
S-O2	1.351 (9)	P-C13	1.795 (7)
		P-C19	1.814 (7)
		C19-C20	1.509 (9)
I-S-O1	105.7 (4)	C1-P-C7	109.0 (3)
I-S-O2	102.1 (5)	C1-P-C13	111.2 (3)
O1-S-O2	113.7 (8)	C1-P-C19	104.7 (3)
		C7-P-C13	108.5 (3)
		C7-P-C19	113.1 (3)
		C13-P-C19	110.4 (3)
		P-C19-C20	117.1 (5)

^a The average C-C distances and C-C-C angles within individual phenyl rings were 1.385 Å and 120.0 deg, respectively. The P-C-C angles were 117.1-120.9°.

completely decolorized above 100 °C, and subsequently melt near the melting point of the corresponding iodide salt.

Results of tensimetry experiments for some of the complexes are given in Table II. Pressure-temperature plots were generally well behaved for the iodosulfates in the 0-100 °C range (in contrast to $L_m\text{CuI-SO}_2$ systems, which exhibited some complications due to ligand dissociation¹²) and thus the enthalpies for the dissociation reactions are reasonably well defined. The SO_2 pressures are in the range 0.5-13 Torr at ambient temperature, and estimated dissociation enthalpies are 5-19 kcal/mol. These values are similar to those observed for $L_m\text{CuI-SO}_2$ systems and for several $L_m\text{M-SO}_2$ systems.^{12,19} The selenocyanate- and thiocyanate- SO_2 adducts decomposed on heating.

Frequencies for SO_2 vibrations are given in Table II. For the iodosulfates, the bend occurs at 514-531 cm^{-1} , the asymmetric stretch at 1264-1300 cm^{-1} , and the symmetric stretch at 1087-1123 cm^{-1} . Ligand vibrations often complicated SO_2 frequency assignments in the infrared. However, the Raman spectrum allowed the symmetric S-O stretch to be assigned unambiguously since in almost every case this mode was the strongest Raman band observed. The frequency ranges for $\nu_s(\text{S=O})$ and $\nu_{as}(\text{S=O})$ have been shown to be useful diagnostics in defining the mode of SO_2 complexation as being

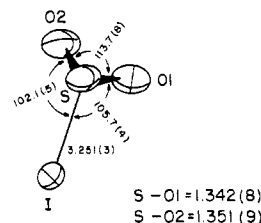
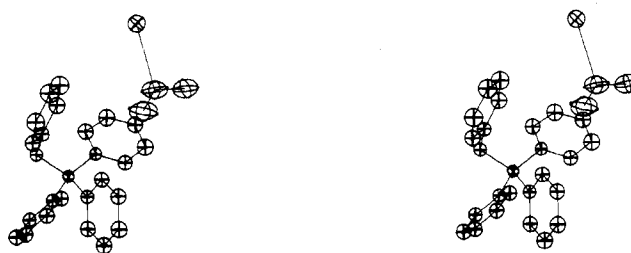


Figure 1. The structure of the iodosulfate anion.

Figure 2. Stereoplot of the structure of $[\text{PPh}_3\text{Bz}](\text{ISO}_2)$.

M-SO_2 (coplanar), M-SO_2 (pyramidal), or M-L-SO_2 (pyramidal),²⁰ and the frequencies observed in the present study clearly fall into ranges defined by the latter structural category.

The structure of the iodosulfate ion is shown in Figure 1 and a stereoplot of the structure of $[\text{PPh}_3\text{Bz}](\text{ISO}_2)$ is given in Figure 2. The structure consists of discrete, well-separated $[\text{PPh}_3\text{Bz}]$ cations and ISO_2 anions. As expected, the iodosulfate anion is pyramidal ($\text{I-S-O} = 102.1 (5), 105.7 (4)^\circ$; $\text{O-S-O} = 113.7 (8)^\circ$; the angle between the SO_2 plane normal and the I-S vector = 26.2°). The O-S-O angle is insignificantly different from that in gaseous SO_2 and many SO_2 complexes, but the S-O distances, 1.342 (5), 1.351 (9) Å, are much shorter than the 1.40-1.45 Å usually found in well-determined SO_2 structures.¹⁵ The shortening is probably an artificial one due to the large vibrational amplitudes for the oxygens in the present structure. The I-S distance, 3.251 (3) Å, is much longer than the sum of covalent radii (2.36 Å) but shorter than the I-S distance (3.39-3.41 Å) found in $\text{Pt}(\text{PPh}_3)_2(\text{CH}_3)\text{I-SO}_2$ and $\text{Cu}_2(\text{PPh}_3\text{Me})_4\text{I}_2\text{SO}_2$ and shorter than

the sum of van der Waals radii (3.78 Å).^{11,12} No other I-S distances of any type appear to have been reported. Burow's normal-coordinate analysis for ISO_2^- assumed a much shorter I-S distance of 2.5 Å.⁸ No unusual features were evident in the triphenylbenzyl cation or the crystal packing.

Conclusions

The use of large organo cations allows convenient synthesis of a series of well-defined, easily handled iodosulfinate complexes. The complexes have SO_2 dissociation pressures in the range 0.5–17 Torr at ambient temperature and SO_2 dissociation pressures in excess of 1 atm at 100 °C and higher. The geometry of the ISO_2^- anion has been shown by x-ray diffraction to be pyramidal with an I-S distance of 3.251 (3) Å.

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Registry No. [K(18-crown-6)](ISO_2), 65392-62-3; [Rb(18-crown-6)](ISO_2), 65392-61-2; [AsPh₄](ISO_2), 65392-60-1; [PPh₃Bz](ISO_2), 65392-59-8; [Ph₃P-N-PPh₃](ISO_2), 65392-58-7; [Na(18-crown-6)](NCSO₂), 65392-57-6; [K(18-crown-6)]-

(NCSO₂), 65392-56-5; [K(18-crown-6)]I₃, 65392-54-3.

Supplementary Material Available: A listing of structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

References and Notes

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Molybdenum and Rhenium Complexes of Aromatic Amine Thiolate Ligands

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Complexes of the form $\text{Mo}(\text{C}_6\text{H}_3\text{XSNH})_3$ (X = H, Cl) are prepared by reaction of the *o*-aminobenzenethiol ($\text{C}_6\text{H}_3\text{XSHNH}_2$) either with MoO_4^{2-} in acidic aqueous ethanol or with $\text{MoO}_2(\text{acac})_2$ in CH_3OH . The N-deprotonation, established by analytical and spectroscopic studies, illustrates the acidity enhancement effect of metals in high formal oxidation states. The observation of ¹H and ¹⁴N superhyperfine splitting in the EPR spectrum of $\text{Mo}(\text{C}_6\text{H}_3\text{SNH})_3^-$ prepared in situ from $\text{Mo}(\text{C}_6\text{H}_3\text{SNH})_3$ confirms the protonation state of the ligands. Reaction of ReO_4^- and $\text{C}_6\text{H}_3\text{XSHNH}_2$ under similar conditions yields complexes of tentative formulation $\text{Re}(\text{C}_6\text{H}_3\text{XSNH})_2(\text{C}_6\text{H}_3\text{XSN})$ from which $\text{Re}(\text{C}_6\text{H}_3\text{XSNH})_3^+$ complexes can be prepared where $n = 1-, 0, 1+$. The complex with charge $1+$ is only stable in acid solution. Both Mo and Re complexes show reversible electron-transfer behavior in polar aprotic solvents, and their electronic spectra indicate a close resemblance to tris(1,2-dithiolene) complexes which possess trigonal-prismatic coordination. Incorporation of the *o*-aminobenzenethiolate unit into tetradentate ligands, L = $\text{C}_6\text{H}_4(\text{S}^-)\text{NHCHRCHRNHC}_6\text{H}_4(\text{S}^-)$ (R = H, CH₃), allows preparation of Mo(VI) complexes of the form MoO_2L and $\text{Mo}_2(\text{SC}_6\text{H}_4\text{NCH}_2\text{CH}_2\text{NC}_6\text{H}_4\text{S})_3$, the latter spectroscopically resembling the tris complexes reported above. The observed EPR properties and the ability of some of these complexes to transfer both electrons and protons are discussed in relation to the possible role of molybdenum in enzymes.

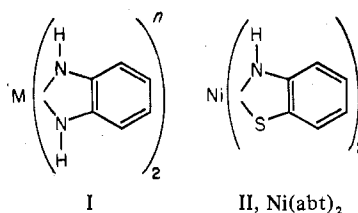
Introduction

The unsaturated 1,2-dithiolate ligands (1,2-dithiolenes²) have been found to form bis,^{2,3} tris,^{2,4-6} and tetrakis⁷ complexes which display an array of interesting chemical, electrochemical, structural, and electronic structural properties. In particular, the tris complexes display reversible electron-transfer properties⁴⁻⁶ and structural variation⁸⁻¹³ as a function of metal, ligand, and oxidation state. For a given metal, the more highly oxidized members of an electron-transfer series display trigonal-prismatic coordination while the reduced members show structures closer to the octahedral geometry.^{6,9,10} Similarly, as one moves from right to left (e.g., from Mo to Zr) in the periodic table, the tendency to adopt trigonal-prismatic coordination decreases.¹¹⁻¹³

Certain unsaturated amine and amine thiol ligands¹⁴⁻¹⁸ display many of the properties of the dithiolenes. For example,

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a series of complexes, I, has been prepared from *o*-



phenylenediamine¹⁷ for M = Co, Ni, Pd, and Pt; $n = 0, 1+$. In these complexes each amine group is monodeprotonated and functionally is a coordinated amido group. Additionally, the oxidized complex of nickel and *o*-aminobenzenethiol, II, $\text{Ni}(\text{abt})_2$, has also been shown^{14,15} to contain monodeprotonated amine groups and to have dithiolene character.

In contrast, this same ligand, *o*-aminobenzenethiol, also forms a series of more conventional complexes wherein the amine retains its fully protonated form. Larkworthy et al.¹⁹