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Synthesis and Stereochemistry of Homoleptic Transition Metal Thiobenzoate Complexes, $(Ph_4P)[M(SC\{O\}Ph)_3]$ (M = Mn, Co, and Ni)†

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Introduction

The chemistry of metal-thiocarboxylates has not been explored extensively, as compared to that of metal thiolates.[1] However, the $RC\{O\}S^-$ anions constitute an interesting class of ligands having a soft sulfur donor site and a hard oxygen donor site. Recently we have begun a systematic exploration of the ligand chemistry of the thiobenzoate anion, $PhC\{O\}S^-$. The ability of the ligand to bind to both hard and soft metals has been demonstrated in the structure of $\{Na[Cd(SC\{O\}Ph)_3]_2\}^-$ anion in which the relatively soft Cd(II) ion is bonded strongly to the sulfur atoms while the hard Na (I) ion is attached to the oxygen atoms.[2] All three divalent group 12 elements form anions $[M(SC\{O\}Ph)_3]^-$, in which the metal atoms are surrounded by three sulfur atoms in a trigonal planar fashion[3], with much weaker M···O bonding. This trigonal planar geometry appears to be independent of the nature of counterions and hydrogen bonding effect.[4,5] Very lately, we have also found a different, trigonal pyramidal stereochemistry around Cd in two of the three crystallographically different anions in rhombohedral $(Ph_4P)[Cd(SC\{O\}Ph)_3]$.[6] In the case of triligated Sn(II) and Pb(II) complexes, a trigonal pyramidal geometry was observed with weak or no interactions between the O atoms of carbonyl groups and the central metal ions.[7,8] These structural differences are presumably controlled by the nature of the metal ions, most obviously by the presence of a stereochemically active lone pair in the Sn(II) and Pb(II) complexes. Recently, Hampden−Smith et al. have prepared group 12 metal thiocarboxylates of the type $[M(SC\{O\}R)_2Lut_2]$ (where M = Zn, Cd, R = Me, $C(CH_3)_3$, Lut = 3,5-dimethylpyridine) as precursors to metal sulfide materials.[9] Further, indium and tin thiobenzoate complexes have been reported.[10] However, apart from simple neutral metal−thiobenzoates,[11] to our knowledge no other homoleptic transition metal(II) thiobenzoato complexes have been reported. The transition metal(II) ions are expected to exhibit variable coordination numbers, and it was thought interesting to synthesize thiobenzoate complexes and study their stereochemical features. Reported here are the syntheses and structural properties of the first homoleptic thiobenzoato complexes of Mn(II), Co(II), and Ni(II).

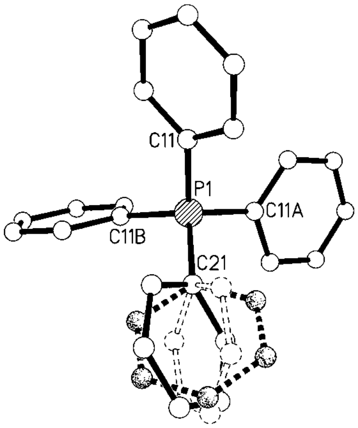

Figure 1. A ball-and-stick diagram of the disordered Ph_4P^+ in **1**.

Results and Discussion

Syntheses. The anions $[M(SC\{O\}Ph)_3]^-$ (M = Mn, Co, Ni) were synthesized from an appropriate metal salt and Et_3NH^+ $PhC\{O\}S^-$ (produced in situ from $PhC\{O\}SH$ and Et_3N), as given by eq 1.

$$M^{2+} + 3\ PhC\{O\}S^- \rightarrow [M(SC\{O\}Ph)_3]^- \qquad (1)$$

These monoanions were isolated as the Ph_4P^+ salts. Under our experimental conditions, no tetrakis(thiobenzoato) or higher complexes were obtained.

Structures of $(Ph_4P)[M(SC\{O\}Ph)_3]$ (M = Mn, (**1**), Co, (**2**), Ni, (**3**)). The crystal and molecular structures were determined by single-crystal X-ray diffraction techniques. The crystal structures of **1**−**3** consist of discrete cations and anions. All three compounds crystallized in the same trigonal space group *R*3. Both anions and cations have crystallographically imposed C_3 symmetry. As a consequence, one phenyl ring (C_{21}−C_{26}) of the Ph_4P^+ was disordered (Figure 1). Disorder of Ph_4P^+ is uncommon since these cations are usually locked into place by specific cation−cation interactions.[12]

In the anions, the metal atoms are situated on the C_3 axis, and the three $PhC\{O\}S^-$ ligands are related by 3-fold rotational symmetry. The structure of a representative anion in **3** is shown in Figure 2. Selected bond distances angles and interplanar

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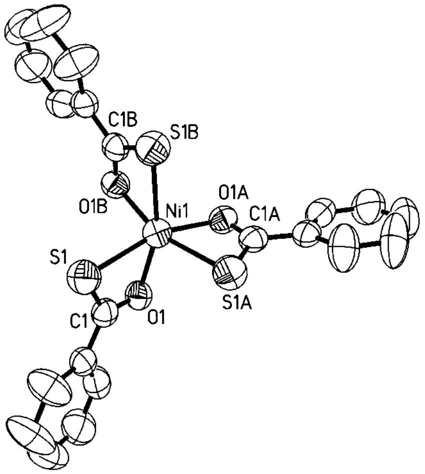

Figure 2. An ORTEP diagram of the anion $[Ni(SC\{O\}Ph)_3]^-$ with 50% probability thermal ellipsoids and the numbering scheme. The hydrogen atoms are omitted for clarity.

Table 1. Selected Molecular Geometric Parameters (distances, Å, and angles, deg)

	Mn	Co	Ni
Bond distances			
M−S	2.576(2)	2.468(2)	2.419(1)
M−O	2.214(4)	2.139(3)	2.100(2)
S−C	1.702(6)	1.706(5)	1.705(4)
O−C	1.264(6)	1.241(5)	1.260(4)
Bond angles			
S−M−S	104.41(6)	103.54(6)	102.57(4)
O−M−O	95.6(1)	95.8(1)	95.96(9)
O−C−S	120.0(4)	119.3(4)	118.1(3)
O−M−S	64.6(1)	66.91(8)	68.35(7)
M−S−C	75.7(2)	75.2(2)	75.5(2)
M−O−C	98.9(3)	98.0(3)	97.5(2)
dihedral angle between MSOC planes	83.28(9)	85.83(9)	86.74(7)
dihedral angle between phenyl ring and COSM plane	14.1(3)	13.4(3)	13.2(2)
distance of M from S_3 plane	1.054(2)	1.039(2)	1.050(1)
distance of M from O_3 plane	1.146(4)	1.103(3)	1.079(2)

angles are given in Table 1. The sulfur and oxygen atoms from each thiobenzoate ligand are bonded to the central metal atom to provide a distorted octahedral coordination geometry. For MS_3O_3 kernel two types of geometry are possible namely, *fac* and *mer*. The anions in the present study are found to occur as the *fac* geometry. The geometry around the metal is somewhat similar to that observed[6] in one of the crystallographically independent anions of rhombohedral $(Ph_4P)[Cd(SC\{O\}Ph)_3]$. However, in this anion, which has the C_3 symmetry, the Cd−S bond distances are shorter than the Cd−O distances. The geometry of the anions in **1**−**3** is quite different from that found[3] in $(Ph_4P)[Zn(S\{O\}CPh)_3]$, where the anion has a near-planar ZnS_3 kernel and two long Zn···O interations. The M−O bond lengths and the M−S bond lengths were found to increase in the same order as the size of the metal ions, which are high-spin for M = Mn and Co (see Experimental Section), i.e., Mn(II) > Co(II) > Ni(II). The S−M−S angles vary in the same order, while the O−M−O angles show the reverse order, although in this case the differences are not significant. In the distorted octahedral geometry of the anion, the metal ion is sandwiched between the O_3 and the S_3 planes. It may be noted that the distances of M from the O_3 and the S_3 planes do not differ significantly. The twist angles between the S_3 faces and the O_3 faces are 34(1), 39(1), and 39(1)° for **1**, **2**, and **3**, respectively, partway between 60° expected for an ideal octahedron and 0° for an ideal trigonal prism. In the $PhC\{O\}S^-$ ligand, the COS planes are twisted from the planes of the associated phenyl groups.

The anion is chiral. It is interesting to note that in all the three structures, the anions have the Λ-form, as confirmed by refining their Flack parameters. The identical chiralities probably result from serendipitous crystal picking. The bulk compounds did not show any optical activity in CH_2Cl_2 solution.

X-ray powder diffractometry of **1**, **2**, and **3** gave patterns consistent with expectation based on the crystal structure data. Within experimental errors, it may be concluded that the bulk compositions are consistent with the determined structures, and that the bulk contains anions with the *fac* geometry only.

Experimental Section

All the materials used in the syntheses were obtained commercially and used as received except that solvents were dried over 3 Å molecular sieves. All the preparations were carried out under N_2. X−ray powder patterns were obtained using a D5005 Siemens X−ray Diffractometer. Magnetic moments were determined with the aid of a Johnson Mathey Magnetic Susceptibility Balance. Optical activities in solution were determined using a Perkin-Elmer 341 polarimeter. The Microanalytial laboratory at NUS performed microanalyses.

$(Ph_4P)[Mn(SC\{O\}Ph)_3]$ (1). Triethylamine (4.20 mL, 0.03 mol) in methanol (20.0 mL) was added dropwise to a solution of thiobenzoic acid (4.516 g, 0.03 mol) in methanol (30.0 mL). $MnCl_2{\cdot}4H_2O$ (1.926 g, 0.01 mol) in methanol (10.0 mL) was then added. The solution turned from yellow to orange-yellow. Ph_4PBr (4.082 g, 0.01 mol) in methanol (20.0 mL) was added dropwise from a syringe. A yellow precipitate was observed to have formed halfway through the addition. Dichloromethane (90.0 mL) and ethyl acetate (5.0 mL) were added together with heating to dissolve the precipitate. The solution was placed in the refrigerator overnight for crystallization to occur. Orange crystals were obtained. The mother liquor was removed, and the crystals were then dried under nitrogen. (Yield 2.7 g, 34.6%). Anal. Calcd for $C_{45}H_{35}O_3S_3MnP$ (mol wt 805.82): C, 67.07; H, 4.38; S, 11.94. Found: C, 66.30; H, 4.44; S, 12.26. Magnetic moments, 5.99 μ_B.

$(Ph_4P)[Co(SC\{O\}Ph)_3]$ (2). This preparation was essentially the same as that of **1**. However, the amounts of starting materials were as follows: $PhC\{O\}SH$, 2.0 mL, 0.0153 mol; Et_3N, 2.13 mL, 0.0153 mol; $Co(NO_3)_2{\cdot}6H_2O$, 1.483 g, 0.005 mol; PPh_4Br, 2.145 g, 0.005 mol. The yield of the greenish-brown precipitate was 2.490 g, 60.2%. Anal. Calcd for $C_{45}H_{35}O_3S_3CoP$ (mol wt 809.91) C, 66.74; H, 4.36; S, 11.88. Found: C, 65.87; H, 4.20; S, 12.10. Magnetic moments, 4.67 μ_B.

$(Ph_4P)[Ni(SC\{O\}Ph)_3]$ (3). The synthesis was similar to that of **2**. The materials used were as follows: $PhC\{O\}SH$, 0.693 g, 0.0045 mol; Et_3N, 0.63 mL, 0.0045 mol; $NiCl_2{\cdot}6H_2O$, 0.215 g, 0.0009 mol; PPh_4Br, 0.378 g, 0.0009 mol. The yield for the yellowish-brown precipitate obtained was 0.663 g, 90.4%. Anal. Calcd for $C_{45}H_{35}O_3S_3NiP$ (mol wt 809.59): C, 66.76; H, 4.36; S, 11.88. Found: C, 66.25; H, 4.16; S, 11.70. Magnetic moments, 2.96 μ_B.

Single crystals of **1** were obtained during synthesis whereas for **2** and **3**, they were obtained by the diffusion method from a CH_2Cl_2 solution and ethyl acetate at 5 °C and room temperature, respectively.

X-ray Structure Determinations. The diffraction experiments were carried out on a Siemens SMART CCD three-circle diffractometer with a Mo Kα sealed tube at 23 °C. The softwares used were as follows: SMART[13] for collecting frames of data, indexing reflection, and determination of lattice parameters; SAINT[13] for integration of intensity of reflections and scaling; SADABS[14] for absorption correction; and SHELXTL[15] for space group determination, structure solution, and least-squares refinements on F^2. In the trigonal crystal system, between

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(13) SMART & SAINT Software Reference Manuals, Version 4.0, Siemens Energy & Automation, Inc., Analytical Instrumentation, Madison, WI, 1996.

(14) Sheldrick, G. M. SADABS a software for empirical absorption correction, University of Gottingen, Gottingen, Germany, 1996.

(15) SHELXTL Reference Manual, Version 5.03, Siemens Energy & Automation, Inc., Analytical Instrumentation, Madison, WI, 1996.

Table 2. Summary of Crystallographic Data for **1**−**3**

	1	**2**	**3**
chemical formula	$C_{45}H_{35}MnO_3PS_3$	$C_{45}H_{35}CoO_3PS_3$	$C_{45}H_{35}NiO_3PS_3$
formula weight	805.82	809.81	809.59
space group		*R*3 (no. 146)	
T, °C		20	
λ, Å		0.71073	
a, Å	13.2996(5)	13.2775(2)	13.2343(3)
c, Å	19.934(1)	19.8742(5)	19.7741(2)
V, Å^3	3053.5(2)	3034.3(1)	2999.36(7)
Z		3	
ρ_{calc}, g cm^{-3}	1.315	1.330	1.345
μ, cm^{-1}	5.60	6.58	7.21
$R1$ [$I \geq 2\sigma(I)$][a]	0.0532	0.0399	0.0462
$wR2$ [$I \geq 2\sigma(I)$][b]	0.1315	0.0795	0.0961

[a] $R1 = (||F_o| - |F_c||)/(|F_o|)$. [b] $wR2 = [(w(F_o^2 - F_c^2)/(wF_o^4]^{1/2}$.

centric- and noncentric space groups, the choice of the chiral space group *R*3 was based on E^2 statistics. Successful solution and refinement of the structure confirmed the correctness of the choice. For $Z = 3$, there is a crystallographically imposed C_3 symmetry present in the Ph_4P^+ cation, and the P and C_{21} of Ph_4P^+ are on the C_3-axis. As a consequence, this phenyl ring is crystallographically disordered. The disordered rings were resolved successfully and modeled, and constraints were applied to keep the ideal symmetry of the phenyl ring. A riding model was used to place the hydrogen atoms in their idealized positions. The crystal of **2** was found to be twinned by merohedry. The twin matrix 010, 100, 00-1 was used, and the batch scale factor for this twin matrix was refined to 0.445(2). A brief summary of the crystallographic data is given in Table 2.

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Supporting Information Available: Observed and simulated X-ray powder patterns for complexes (**1, 2** and **3**) have been deposited (6 pages). X-ray crystallographic files in CIF format for complexes **1**, **2** and **3** are available on the Internet only. Ordering and access information is given on any current masthead page.

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