Lorentzian line shapes are 10.2 and 7.5 G, respectively. At 80 mM $Cr(ox)_3^{3-}$ and 80 mM $Fe(CN)_6^{3-}$ the line widths are 33 and 14 G, respectively. In all cases the integrated intensity of the nitroxyl spectrum was independent, within experimental uncertainty, of the concentration of the metal ion added.

Conclusion

$Cr(ox)_3^{3-}$ is a more effective broadening agent for the tempamine nitroxyl radical than is $Fe(CN)_6^{3-}$. The optimum conditions for use in aqueous solutions are pH <8 and low buffer concentrations. It is more effective in Tris buffer than in phosphate buffer. The background signal for $Cr(ox)_3^{3-}$ near $g = 2$ is small compared to the nitroxyl signals.

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Registry No. $Cr(ox)_3^{3-}$, 15054-01-0; $Fe(CN)_6^{3-}$, 13408-62-3; tempamine, 14691-88-4.

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High-Pressure Phase Transformation of Platinum Sulfide

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PtS was found to undergo a high-pressure phase transformation at 30 kbar to a phase isomorphous with PdS. The ambient and high-pressure phases are diamagnetic semiconductors with electrical band gaps of 0.32 and 0.19 eV, respectively. The extent of solid solution of NiS in both phases of PtS was found to be less than 10 atom %.

Introduction

PtS, the mineral cooperite, adopts a tetragonal structure (Figure 1), space group $P4_2/nmm$, in which each Pt atom forms four coplanar bonds to bridging sulfur atoms.[1] The Pt–S bonds form the sides of large open channels that extend along the *a* directions. These channels are not retained in the closely related but less symmetric structure of PdS,[1] space group $P4_2m$ (Figure 2). A more compact structure for PdS is also indicated by a comparison of packing densities: 1 formula unit/34.1 Å^3 for PdS and 1 formula unit/36.8 Å^3 for PtS. In addition, the mineral braggite, (Pt, Pd, Ni)S, for which the Pt content is greater than that of Pd and Ni crystallizes in the PdS structure.[2] These observations suggested that PtS would under high pressure transform to a phase with the PdS structure. It was also of interest to determine the extent of substitution of other transition metals, i.e., Pd, Ni, Co, and Cr, for Pt and the effect of these substitutions on the phase transformation.

Experimental Section

Sample Preparation. All samples were prepared by the direct reaction of high-purity (>99.99%) elements in evacuated silica tubes at 750 °C. These samples were heated for at least 130 h with several intermittent grindings. After each heat treatment, they were cooled to room temperature at a rate of 100 °C/h. $Pt_{1-x}M_xS$ (M = Ni, Cr, Co, Cu) reacted samples were subjected to pressures between 25 and 50 kbar for $^1/_2$ h at a temperature of 1000 °C in a belt apparatus of the type described by Hall.[3]

When a sample of NiS was cooled to room temperature at the cooling rate employed above, the millerite phase was obtained. Quenching to room temperature yielded NiS with the NiAs structure as reported previously.[4] The two modifications of NiS are a high-temperature phase with the NiAs structure and the millerite phase which is stable below 380 °C.

Sample Characterization. X-ray Crystallography. Powder patterns were recorded with a Norelco X-ray diffractometer equipped with a high-intensity copper source (λ(Cu Kα_1) = 1.5405 Å) and with a graphite monochromator located in the diffracted beam. Scan rates of 1 and $^1/_4$°/min were employed to obtain patterns for phase identifications and to collect data for lattice parameter determinations, respectively. The lattice parameters reported for each sample were determined from a least-squares refinement using 2θ angles between 50 and 140° corrected with reference to an Si internal standard.

Density Measurements. Densities were measured by a hydrostatic technique previously described by Adams.[5] Perfluoro(1-methyldecalin) calibrated with a high-purity silicon crystal (ρ = 2.328 g/cm^3) was employed as the density fluid.

Magnetic Measurements. Magnetic susceptibilities were determined over a temperature range of 77–300 K with a Faraday balance described by Morris and Wold.[6] No corrections were applied for core diamagnetism.

Electrical Measurements. Resistivity measurements were performed by the four-probe technique developed by van der Pauw.[7] Ohmic contacts were made with indium using an ultrasonic soldering device (12-W generator, Sonobond Corp.).

Results

PtS transformed completely to a high-pressure phase, PtS(p), at 30-kbar pressure and 1000 °C in $^1/_2$ hour. At 25 kbar this transformation was incomplete. Comparison of the powder patterns of PtS(p) and PdS confirmed that PtS(p) is isomorphous with PdS. Lattice parameters and densities for the two phases are given in Table I. Also listed for comparison are the lattice parameters of PtS, PdS, and braggite reported previously.[2,8,9]

Both the ambient and high-pressure phases of PtS are diamagnetic. The measured susceptibility at room temperature for PtS prepared at ambient pressure is −0.15 emu/g. At liquid nitrogen temperature the susceptibility is slightly field-strength dependent. Grønvold et al. also observed this behavior and reported a room-temperature diamagnetic susceptibility equal to that given here.[8] For PtS(p) similar results were obtained; the diamagnetic susceptibility measured at room temperature is −0.11 emu/g.

PtS and PtS(p) are narrow band gap semiconductors. A plot of log ρ vs. $10^3/T$, where ρ is sample resistivity, is shown in Figure 3 for these phases. For PtS, measurements were made on a cold-pressed bar sintered at 975 °C; the PtS(p)

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Table I. Lattice Parameters and Densities

compd	ref	a, Å	c, Å	ρ_{exptl}, g/cm^3	ρ_{calcd}, g/cm^3
PtS	this work	3.4697 (2)	6.1099 (3)	10.21 (3)	10.26
	8	3.4700	6.1096	11.15 (3)	11.14
PtS (p)	this work	6.409 (1)	6.596 (1)		
braggite	2	6.380	6.570		
PdS	9	6.4287	6.6082		

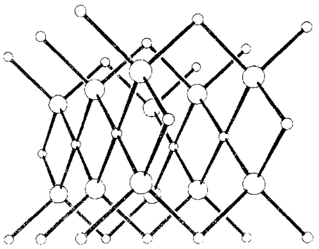

Figure 1. View of PtS showing a channel in an a direction.

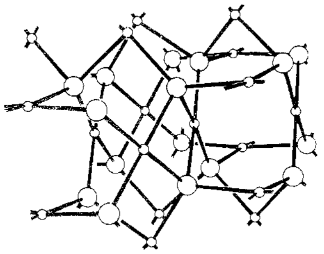

Figure 2. View of PdS indicating that the channels in PtS are not retained in the PdS structure.

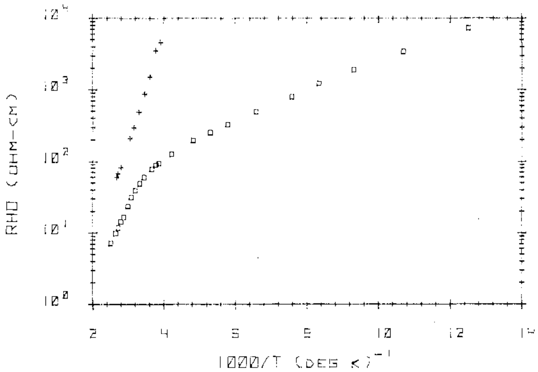

Figure 3. Resistivity of ambient (+) and high-pressure (□) (50 kbar) phases of PtS as a function of temperature.

material was suitable for measurements without modification. Electrical activation energies of 0.32 eV for PtS and 0.19 eV for PtS(p) were calculated from the resistivity data. Whereas grain boundaries affect the values for absolute resistivities, the activation energies are independent of grain boundaries and hence the difference in the values reported for the two phases is meaningful. These activation energies are different from the optical band gap of approximately 0.8 eV for PtS.[10]

Attempts to substitute Cr, Co, and Cu for Pt in PtS and PtS(p) were unsuccessful. Charges of Pt, Cr, and S always yielded three phases: PtS, Cr_2S_3, and Pt. Pd did not substitute for Pt in PtS; substitution in PtS(p) could not be determined since PtS(p) and PdS diffraction peaks overlap even at high 2θ angles.

In the system $Pt_{1-x}Ni_xS$, x can have values less than 0.1. Evidence for such solid solutions is shown in Figure 4, which relates the shifts in the lattice parameters as a function of x. Only the most intense peak of NiS (NiAs type), (100), appeared in the diffraction pattern of the $x = 0.1$ reacted powder in addition to peaks of $Pt_{1-x}Ni_xS$. For compositions with $x > 0.1$, additional peaks for NiS were detected; for $x = 0.05$ and 0.025, no NiS peaks were observed.

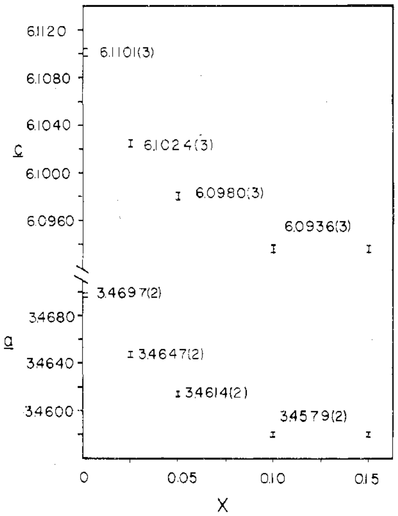

Figure 4. Lattice parameters for $Pt_{1-x}Ni_xS$.

Table II. Room-Temperature Magnetic Susceptibility for $Pt_{1-x}Ni_xS$ Samples

sample	χ, emu/g
NiS	2.29×10^{-6}
0.9 PtS:0.1 NiS mechanical mixture	
measd	0.09
calcd ($0.9 \times \chi_{PtS} + 0.1 \times \chi_{NiS}$)	0.09
reacted powders	
$Pt_{0.9}Ni_{0.1}S$	−0.05
$Pt_{0.95}Ni_{0.05}S$	−0.12
PtS	−0.15
reacted powders subjected to pressure of 50 kbar	
$x = 0.1$	−0.10
$x = 0.05$	−0.13
PtS(p)	−0.11

Magnetic susceptibility measurements at room temperature also indicate Ni substitution in PtS. NiS, crystallizing with the NiAs structure type, is Pauli paramagnetic above 264 K.[11] The susceptibility of a NiS sample measured 2.29×10^{-6} emu/g which is in agreement with that obtained by Sparks and Komoto, 2.24×10^{-6} emu/g.[12] In NiS, d^8 Ni, which is located on an octahedral site, has a high spin state configuration. However, low spin state d^8 Ni may be expected for square-planar coordination. Hence, a $Pt_{1-x}Ni_xS$ solid solution in which all the cations are square planar should be diamagnetic. Thus, it can be seen from Table II that the susceptibility of the sample $Pt_{0.9}Ni_{0.1}S$, -0.05×10^{-6} emu/g, is less than that of a mechanical mixture of 0.9 PtS:0.1 NiS, 0.09 $\times 10^{-6}$ emu/g; and the susceptibility of $Pt_{0.95}Ni_{0.05}S$, -0.12×10^{6} emu/g, is close to that of PtS, -0.15×10^{-6} emu/g.

The Ni-substituted PtS-reacted powders were subjected to pressures up to 50 kbar. Ni has no apparent effect on the phase transformation. Furthermore, for $x = 0.1$ the NiS (100) peak observed in the product prepared at ambient pressure remained unchanged. Hence, no additional solubility of NiS in PtS is observed in the high-pressure phase. Poor resolution at high 2θ angles precluded the detection of shifts in lattice parameters for the high pressure phase samples; however, the magnetic susceptibility measurements suggest retention of Ni in the PtS(p) phase.

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Registry No. PtS, 12038-20-9; NiS, 16812-54-7; cooperite, 12197-03-4.

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A Distorted Tetrahedral Copper(II) Complex of a Tetradentate Schiff Base Ligand

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The reaction of the ligand formed by the 2:1 molar condensation of salicylaldehyde with $\alpha,\alpha,\delta,\delta$-tetramethylputrescine with copper(II) results in the formation of the title compound, referred to hereafter as Cu(sal$_2$tmput). The crystal and molecular structure has been determined using single-crystal X-ray diffraction. The crystal is of the monoclinic class, space group *Cc*, with a = 14.374 (7) Å, b = 14.508 (3) Å, c = 19.370 (3) Å, β = 94.33 (8)°, and Z = 8. The asymmetric unit consists of two independent Cu(sal$_2$tmput) molecules having D_{2d}-distorted tetrahedral symmetry. The dihedral angles defined by the phenyl moieties bound to the copper atoms of the asymmetric pair are 52.4 and 45.6°, respectively. The distortion from the normal square-planar coordination markedly influences the chemical properties of the complex.

Introduction

Coordination complexes with substituted salicylaldehyde ligands have shown a diversity of structures and properties involving a number of stereochemistries and a wide range of bonding interactions.[2,3] Schiff base complexes are of particular interest to inorganic chemists because their structural, spectral, chemical, and electrochemical properties are often strongly dependent on the detailed ligand structure. Schiff base complexes of copper are specifically of interest in bioinorganic chemistry since these complexes provide inorganic models for copper proteins.[4,5]

The structure of Cu(sal$_2$tmput) has been determined as a part of a study of the effects of ligand structure on the chemical properties of Schiff base–metal complexes.[6,7] Of particular interest are comparisons of stereochemistry and electrochemical properties among Schiff base complexes of similar structure, e.g., bis(*N-tert*-butylsalicylaldiminato)copper(II), Cu(*t*-Bu-sal)$_2$,[8,9] (*N,N'*-ethylenebis(salicylideniminato)copper(II), Cu(sal$_2$en),[10] and Cu(sal$_2$tmput).

Experimental Section

General Data. Microanalyses were carried out by the Australian National University Microanalysis Service. Visible–near-infrared spectra were measured on a Cary 14 spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer. The spectra were run as Nujol mulls on KBr disks or as KBr pellets. Mass spectra were obtained on an AEI-MS9 instrument at both low and high resolution. Spectroelectrochemical studies were performed as previously described in the literature[7] (0.5 M Et$_4$NBF$_4$/DMF) vs. a standard calomel electrode. Common laboratory chemicals were of reagent grade.

2,5-Bis(salicylaldimino)-2,5-dimethylhexane (sal$_2$tmputH$_2$). Salicylaldehyde (24.42 g, 0.2 mol) was added directly to a solution of 2,5-dimethylhexane-2,5-diamine (tetramethylputrescine) (14.43 g, 0.1 mol) in 150 mL of absolute ethanol. The resulting reaction mixture was refluxed 1 h and allowed to cool. Bright yellow crystals were filtered off, washed twice with absolute methanol, and dried under vacuum (31.43 g, 89%). The product analyzed as $C_{22}H_{28}N_2O_2$. Calcd: C, 74.97; H, 8.01; N, 7.95. Found: C, 74.92; H, 7.76; N, 8.07. ν_{max} 1630, 1580, 1510, 1420, 1287, 1275, 1215, 1162, 1155, 1118, 1032, 980, 955, 943, 920, 885, 870, 800, 760, 745, 630, 568, 442 cm^{-1}. Mass spectrum 352 (60%), 218 (90%), 122 (100%). Mp 115.5–116.8 °C.

Cu(sal$_2$tmput). sal$_2$tmputH$_2$ (3.52 g, 0.01 mol) in 150 mL of absolute ethanol was added to a solution of copper(II) acetate (2.00 g, 0.01 mol) in 150 mL of absolute ethanol. A suspension of LiOH (0.84 g, 0.02 mol) in absolute ethanol was added and the reaction mixture heated to boiling and filtered.

The filtrate was evaporated and cooled to room temperature, yielding large brown crystals (3.67 g, 88%) which were washed with ethanol. The product was recrystallized from hot isopropyl alcohol and washed with heptane. Anal. Calcd for $CuC_{22}H_{26}N_2O_2$: Cu, 15.35; C, 63.82; H, 6.32; N, 6.77. Found: Cu, 15.50; C, 63.34; H, 6.41; N, 6.72. Mp 247–249 °C. ν_{max} 1610, 1540, 1472, 1450, 1405, 1358, 1335, 1195, 1180, 1150, 1130, 1120, 1030, 960, 865, 860, 800, 760, 745, 590, 510, 502, 450, 408 cm^{-1}. Mass spectrum 413 (parent ion), 352 (free ligand).

Crystals suitable for X-ray diffraction studies were grown by dissolving the recrystallized product in a minimal amount of isopropyl alcohol and layering an equal volume of *n*-heptane on the isopropyl alcohol solution. Solvent diffusion produced crystals of suitable quality in 2 to 3 days.

Spectroelectrochemistry. An optically transparent thin-layer electrode (OTTLE)[11] was employed in conjunction with cyclic voltammetry to electrochemically and spectrally characterize Cu(sal$_2$tmput). The compound is reduced by a negative scan initiated at −0.7 V. This couple is assigned as Cu(II) → Cu(I) with $E^{\circ\prime}$ = −0.722 V. vs. SCE, the $E^{\circ\prime}$ being determined[7] by a plot of $E_{applied}$ vs. log [O]/[R]. The system was shown to be reversible under the slow time scale of the OTTLE spectropotentiostatic experiment, where each potential is maintained until equilibrium is reached. Spectra of Cu(sal$_2$tmput) from spectropotentiometric experiments showed λ_{max} at 380 and 410 nm for the Cu(II) and Cu(I) species, respectively, with isosbestic points at 385 and 500 nm.

X-ray Characterization of Cu(sal$_2$tmput). A dark brown crystal of the Cu(sal$_2$tmput) complex was mounted on a glass fiber and precession photographs of the *hk*0, *hk*1, 0*kl*, and 1*kl* layers were taken using Cu Kα radiation. The systematic absences were for *hkl*, *h* + *k* odd, and for *h*0*l*, *l* odd, suggesting possible choices of space group[12]

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