A/-Methylimidazole Mediated Chemistry of Transition Metal Phenylthiolates.
The Isolation of the Perthiolate Salts \[\text{M(N-MeIm)\textsubscript{6}}(\text{S}\textsubscript{2}\text{Ph})\text subtext{2} \]

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Thiolate, Perthiolate, Imidazole, Metal Powders, Oxidation

Salts of the composition \[\text{M(N-MeIm)\textsubscript{6}}(\text{S}\text{Ph})\text subtext{2} \] (M = Mn, Ni; N-MeIm = N-methylimidazole) were prepared by dissolution of the metal powders with N-MeIm solutions of PhS\text subtext{2}. X-ray crystallographic examination established that these salts indeed feature uncoordinated PhS\text subtext{2}. The salts \[\text{M(N-MeIm)\textsubscript{6}}(\text{S}\text{Ph})\text subtext{2} \] (M = Mn, Ni) react with S\textsubtext{8} to give \[\text{M(N-MeIm)\textsubscript{6}}\textsubtext{S}\textsubtext{8} \] via the intermediacy of the perthiolate salts \[\text{M(N-MeIm)\textsubscript{6}}(\text{S}\text{Ph})\text subtext{2} \].

Introduction

Perthiolates, RS\textsubtext{2}–, have already been discussed as intermediates in the oxidation of thiolates to disulfides by elemental sulfur [1]. The sulfur transfer enzyme rhodanese (implicated in ferredoxin biosynthesis) has been proposed to function via a cysteinate-percysteinate cycle [2]. While coordination complexes of perthiolates are well known [3], salts of perthiolates have not been isolated. Recently Benaichouche et al. reported optical spectroscopic and electrochemical evidence for ArS\textsubtext{2}– in solutions prepared by the addition of sulfur to dimethylacetamide solutions of various aryl thiolates [1]. In this report we describe the isolation and structural characterization of such perthiolate salts synthesized using the super-coordinating solvent N-methylimidazole (N-MeIm) [4].

Results and Discussion

Preparation of the metal thiolates

The first subjects of our study were the phenyl thiolates of manganese and nickel. The salts \[\text{M(N-MeIm)\textsubscript{6}}(\text{S}\text{Ph})\text subtext{2} \] were prepared by the oxidation of the metal powders with N-MeIm solutions of PhS\textsubtext{2} (Scheme 1). The Mn compound is colorless while the nickel salt crystallized in both blue or pink forms, depending on the method of crystallization. N-MeIm solutions of the Ni salt show an intense absorption at 304 nm which is consistent with PhS\textsubtext{2}–. Indeed, single crystal X-ray diffraction studies confirm the formula \[\text{M(N-MeIm)\textsubscript{6}}(\text{S}\text{Ph})\text subtext{2} \] consisting of well separated \[\text{M(N-MeIm)\textsubscript{6}} \] and PhS\textsubtext{2}– subunits (M = Ni, Mn) [5, 6]. DMF solutions of \[\text{Ni(N-MeIm)\textsubscript{6}}(\text{S}\text{Ph})\textsubtext{2} \] are very weakly conductive (2.4 vs 72 cm\textsuperscript{2}mol\textsuperscript{-1}ohm\textsuperscript{-1} in N-MeIm) indicating that in the absence of strongly coordinating solvents the PhS\textsubtext{2}– binds to the metal center.

Cobalt and copper metal also dissolve in N-MeIm solutions of PhS\textsubtext{2} (Scheme 1) although these products have not been structurally characterized.

Scheme 1.

\[
\begin{align*}
\text{Mn} & \rightarrow [\text{Mn(N-MeIm)\textsubscript{6}}(\text{S}\text{Ph})\textsubtext{2} \] \overset{\text{S}\textsubtext{8}}{\rightarrow} [\text{Mn(N-MeIm)\textsubscript{6}}\textsubtext{S}\textsubtext{8} \\
\text{Co} & \rightarrow [\text{Co(S}\text{Ph})\textsubscript{2}(\text{N-MeIm})\textsubtext{2} \] \overset{\text{S}\textsubtext{8}}{\rightarrow} [\text{CoS}\textsubscript{4}(\text{N-MeIm})\textsubtext{2} \\
\text{Ni} & \rightarrow [\text{Ni(N-MeIm)\textsubscript{6}}(\text{S}\text{Ph})\textsubtext{2} \] \overset{\text{S}\textsubtext{8}}{\rightarrow} [\text{Ni(N-MeIm)\textsubscript{6}}\textsubtext{S}\textsubtext{8} \\
\text{Cu} & \rightarrow [\text{Cu(S}\text{Ph})\textsubscript{2}(\text{N-MeIm})\textsubtext{2} \] \overset{\text{S}\textsubtext{8}}{\rightarrow} [\text{CuS}\textsubscript{4}(\text{N-MeIm})\textsubtext{4} \\
\text{Greenish blue} [\text{Co(S}\text{Ph})\textsubscript{2}(\text{N-MeIm})\textsubtext{2} \] & is similar in stoichiometry to the known \text{Co(S(S-2,3,5,6-Me\textsubscript{4}C\textsubscript{6}H\textsubscript{12})(2,9-Me\textsubscript{2}-phenanthroline) [7]. Pale yellow} \text{Cu(S}\text{Ph})\textsubscript{2}(\text{N-MeIm})\textsubtext{2} is thought to be polymeric partly because of its stoichiometry and the fact that it dissolves in THF upon the addition of small amounts of N-MeIm. \text{Cu(S}\text{Ph})\textsubscript{2}(\text{N-MeIm})\textsubtext{2} was also found to react with \text{PPh}\textsubtext{3} to give the known \text{Cu(S}\text{Ph})\textsubscript{2}(\text{PPh}\textsubtext{3})\textsubtext{4} [8].
\end{align*}
\]
Analogous oxidations of N-MeIm suspensions of metal powders occur with Ph₂Se₂, e.g. \([\text{M}(\text{N-MeIm})₆](\text{SePh})₂\) and \(\text{Cu}_3(\text{SePh})₃(\text{N-MeIm})₂\).

**Reactions of the metal thiolates with elemental sulfur**

\(\text{N-MeIm}\) solutions of the new metal thiolates are highly reactive towards elemental sulfur yielding polysulfide derivatives (Scheme 1). The \(\text{Ph}_2\text{S}_2\) by-product of these reactions was assayed by gas chromatography. \(\text{N-MeIm}\) solutions of \([\text{M}(\text{N-MeIm})₆](\text{SPh})₂\) react quickly (second, 25 °C) with an excess \(\text{S}_₈\) to give red \([\text{M}(\text{N-MeIm})₆]\text{S}_₈\) for \(\text{M} = \text{Mn}, \text{Ni}\). These salts had been prepared previously by the direct oxidation of metal powders with \(\text{N-MeIm}\) solutions of \(\text{S}_₈\) [4a]. From \([\text{Co}(\text{SPh})₃(\text{N-MeIm})₃]ₙ\) we obtained a brown compound analyzing as \(\text{CoS}_₄(\text{N-MeIm})₂\), a rare example of a cobalt polysulfide complex that merits further investigation. Oxidation of an \(\text{N-MeIm}\) solution of \([\text{Cu}_3(\text{SPh})₃(\text{N-MeIm})₂]\) with excess sulfur gives \(\text{Cu}_₄(\text{S}_₅)₂(\text{N-MeIm})₄\) [4b].

Intermediates in the sulfidation were obtained in the case of the Mn and Ni salts. The reaction of \([\text{Mn}(\text{N-MeIm})₆](\text{SPh})₂\) and \([\text{Mn}(\text{N-MeIm})₆]\text{S}_₈\) in a 3:1 ratio followed by toluene precipitation gave pale green \([\text{Mn}(\text{N-MeIm})₆](\text{S}_₂\text{Ph})₂\). This salt could also be prepared straightforwardly by the partial oxidation of preformed \([\text{Mn}(\text{N-MeIm})₆](\text{SPh})₂\) according to eq. (1).

\[
[\text{Mn}(\text{N-MeIm})₆](\text{SPh})₂ + 2 \text{S} \rightarrow [\text{Mn}(\text{N-MeIm})₆](\text{S}_₂\text{Ph})₂
\]  \hspace{1cm} (1)

In contrast, blue-green crystals of \([\text{Ni}(\text{N-MeIm})₆](\text{S}_₂\text{Ph})₂\) could only be obtained in good yield from the direct reaction of an \(\text{N-MeIm}\) suspension of \(\text{Ni}\) powder, sulfur, and \(\text{Ph}_2\text{S}_₂\). This reaction is accompanied by the formation of black solids which we propose are composed of nickel sulfido clusters. The color of \(\text{N-MeIm}\) solutions of \([\text{Mn}(\text{N-MeIm})₆](\text{S}_₃\text{Ph})₂\) is brown with absorptions at 336 nm and 614 nm, the latter indicating the presence of \(\text{S}_₃^-\) [4a]. Thus, although this Mn salt can be recrystallized, it appears that the \(\text{PhS}_₂^-\) chromophore does not remain intact in solution because of the equilibrium shown in eq. (1).

\[
3 \text{PhS}_₂^- \rightleftharpoons \text{S}_₃^- + 2 \text{PhS}^- + \frac{1}{2} \text{Ph}_₂\text{S}_₂
\]  \hspace{1cm} (1)

**Structure of \([\text{M}(\text{N-MeIm})₆](\text{S}_₂\text{Ph})₂\)**

Single crystal X-ray diffraction established the structures of the 1:2 salts \([\text{M}(\text{N-MeIm})₆](\text{S}_₃\text{Ph})₂\) for \(\text{M} = \text{Mn}\) and \(\text{Ni}\) (Fig. 1). In both cases one observes octahedral \([\text{M}(\text{N-MeIm})₆]^{2+}\) dications with crystallographically imposed centrosymmetry. The \(\text{M}-\text{N}\) distances range from 224.8–229.0(2) pm in the Mn structure and 213.2–215.0(6) pm for the Ni case. The \(\text{M}-\text{N}\) angles are all within 2.5° of 90°. The interesting parts of the structures are the \(\text{PhS}_₂^-\) anions. The \(\text{S}-\text{S}\) distances are slightly short at 202.2(1) (Mn) and 197.8(4) ppm (Ni) (compare orthorhombic \(\text{S}_₈\) at 205 pm) and the \(\text{C}-\text{S}-\text{S}\) angles (108.1(1), 107.6(4)°) are comparable to those in \(\text{Ph}_2\text{S}_₂\) [9]. The \(\text{PhS}_₂^-\) anions are very nearly planar such that, for the crystallographically better defined Mn salt, the terminal S atom is only 5.1 pm outside of the best plane defined by C₁₃–C₁₈ and S₂. Collectively the structural data suggest delocalized \(\pi\)-bonding throughout the \(\text{C}_₆\text{S}_₂\) framework.

**Summary**

\(\text{N-MeIm}\) has been shown to promote the dissolution of metals by \(\text{Ph}_₂\text{S}_₂\). Within the context of metal thiolate chemistry, it is highly unusual to observe thiolates in the role of gegenions. This represents a powerful, direct route to a range of coordination complexes. This work provides structural proof that the oxidation of the mercaptides by sulfur proceeds via perthiolates which can be further oxidized to give organic disulfides and polysulfide anions.

**Experimental**

Infrared data were recorded with a Mattson Galaxy FT IR on KBr pellets and the data are re-

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Fig. 1. Structure of the \(\text{PhS}_₂^-\) anion in \([\text{Mn}(\text{N-MeIm})₆](\text{S}_₃\text{Ph})₂\) with thermal ellipsoids drawn at the 50% probability level.
ported in cm\(^{-1}\). UV-Vis data were recorded on a Hewlett-Packard Model 8452a spectrophotometer and are reported in nm. Solution conductivities were measured with a YSI Incorporated Model 31A conductivity bridge using their Model 3403 cell (cell constant, \(k = 1\)). Concentrations for solution conductivities were \(\sim 1 \times 10^{-3}\) M. Data are reported as cm\(^2\) mohm\(^{-1}\).

Microanalyses were performed by the School of Chemical Sciences Microanalytical Laboratory, University of Illinois at Urbana-Champaign. The inductively coupled plasma technique was used to analyze metals and sulfur using a Perkin-Elmer Elmer II argon ion instrument.

\[\text{[Mn(N-Melm)\textsubscript{6}]S\textsubscript{8} from [Mn(N-Melm)\textsubscript{6}](SPh)\textsubscript{2}}\]

A slurry of 0.271 g Mn (4.95 mmol) and 1.02 g Ph\(_2\)S\(_2\) (5.00 mmol) in 9 ml of N-Melm was stirred at 120 °C for 12 h to give a light brown solution. The solution was filtered and allowed to cool at 5 °C for 2 h. The colorless crystals were washed twice with 15 ml toluene and 15 ml Et\(_2\)O. Yield: 1.85 g (49%). IR: 1572 (s), 482 (m), 419 (m).

Analysis for C\(_{36}\)H\(_{46}\)MnN\(_{12}\)S\(_{7}\)
Calcd C 56.45 H 6.05 N 21.94 Mn 7.17 S 8.37% ,
Found C 56.30 H 6.17 N 22.12 Mn 7.10 S 8.66%.

\[\text{[Ni(N-Melm)\textsubscript{6}]S\textsubscript{8} from [Ni(N-Melm)\textsubscript{6}](SPh)\textsubscript{2}}\]

A slurry of 0.435 g Ni (7.42 mmol) and 1.632 g Ph\(_2\)S\(_2\) (7.47 mmol) in 10 ml of N-Melm was stirred at 100–110 °C. After 8 h, the hot, red-brown solution was filtered and diluted with 20 ml toluene to give 4.85 g pink microcrystals (85%). If the red-brown solution was cooled to room temperature without the addition of toluene, the filtrate solidified to a mass of large blue crystals. IR: 1569, 481, 423. UV-Vis (DMF): 478, 340. Conductivity: 2.4 (DMF), 71.97 (N-Melm).

Analysis for C\(_{36}\)H\(_{46}\)MnN\(_{12}\)S\(_{8}\)
Calcd C 56.18 H 6.02 N 20.79 % ,
Found C 56.16 (5.99) (21.81)

The values in the parentheses were obtained for the purple crystals, the other data are for the blue crystals.

\[\text{Cu}_{4}(SPh)_{3}(N-Melm)_{2}\]

A suspension of 0.218 g Cu powder (3.43 mmol), 5 ml N-Melm, and 0.387 g Ph\(_2\)S\(_2\) (1.77 mmol) was stirred at 100 °C for 2 h resulting in a light yellow solution. Most of the solvent was evaporated under vacuum leaving \(\sim 0.5\) ml of liquid which was diluted with 15 ml THF. Addition of 25 ml hexanes gave a yellow oil. The oil was triturated with 20 ml Et\(_2\)O to give a yellow solid which was further washed with 10 ml Et\(_2\)O and dried under vacuum to produce 0.517 g of yellow powder (73%). IR: 1574 (vs), 481 (s), 423 (w).

Analysis for C\(_{16}\)H\(_{24}\)Cu\(_4\)N\(_8\)S\(_{10}\)
Calcd C 21.27 H 2.68 N 12.41 Cu 28.59% ,
Found C 21.66 H 2.86 N 12.56 Cu 28.59%.

\[\text{Cu}_{4}(S_{5})_{2}(N-Melm)_{4} from Cu_{4}(SPh)_{3}(N-Melm)_{2}\]

A solution of Cu\(_4\)(SPh)\(_3\)(N-Melm)\(_2\) prepared from 0.303 g Cu (4.77 mmol) and 0.533 g Ph\(_2\)S\(_2\) (2.44 mmol) in 6 ml N-Melm solution was treated with 0.385 g sulfur (1.5 mmol), resulting in a dark orange solution. After 2 h, the solution was diluted with 15 ml THF and 25 ml toluene. The solid was washed with two 10 ml portions of Et\(_2\)O to give 0.627 g of orange microcrystals (66%). IR and UV-Vis spectra are identical to samples prepared from elemental copper and sulfur [4b].

Analysis for C\(_{16}\)H\(_{24}\)Cu\(_4\)S\(_{8}\)N\(_{10}\)
Calcd C 21.27 H 2.68 N 12.41 Cu 28.59% ,
Found C 21.66 H 2.86 N 12.56 Cu 28.59%.
[Ni(N-MelM)₆]₂(S₂Ph)₂

A mixture of 0.294 g Ni powder (5.01 mmol), 0.160 g sulfur (4.99 mmol), and 1.091 g S₂Ph₂ (5.00 mmol) in 10 ml N-Melm were heated at 60 °C for 2 days. The solution turned dark brown and a black residue was formed. No Ni was visible on the stir bar. The black solid was filtered off and the filtrate was layered with 20 ml toluene. Greenish blue crystals of [Ni(N-MelM)₆]₂(S₂Ph)₂ formed together with a small amount of a black compound. The [Ni(N-MelM)₆]₂(S₂Ph)₂ dissolves in N-Melm with greenish brown color. UV-Vis (N-Melm): 264, 306, 604 (sh, w), 604 (w).

Analysis for C₃₆H₄₆N₁₂NiS₄
Calcd C 51.87 H 5.56 N 20.15 Ni 7.04 S 15.38%, Found C 52.08 H 5.68 N 20.34 Ni 7.25 S 12.72%.

[Mn(N-MelM)₆]₂(S₂Ph)₂

To a stirred solution of 0.115 g [Mn(N-MelM)₆]S₈ (0.143 mmol) in 10 ml N-Melm, 0.320 g [Mn(N-MelM)₆]₉(SPh)₂ (0.418 mmol) was added. The red solution turned green after 5 min. After 2 h the reaction solution was diluted with toluene which precipitated a small amount of white solid. The filtrate was stored at -10 °C for 2 days, giving light green microcrystals which were washed with ether twice and dried under vacuum.

Recrystallization from N-Melm/Et₂O gave 0.28 g (80%) of [Mn(N-MelM)₆]₉(S₂Ph)₂. The same compound could be prepared by the addition of 2 equiv sulfur to a N-Melm solution of [Mn(N-MelM)₆]₉(SPh)₂ followed by dilution with toluene.

Analysis for C₃₆H₄₆N₁₂MnS₄
Calcd C 52.10 H 5.58 N 20.25 Mn 6.62%, Found C 51.62 H 5.51 N 20.24 Mn 6.56%.

Co(N-MelM)₂(SPh)₂

To a suspension of 0.262 g cobalt powder (4.45 mmol) in 9 ml N-Melm, was added 0.973 g Ph₂S₂ (4.46 mmol). After 17 h at 120 °C the cobalt had all dissolved giving a deep green solution. Diluting the solution with 20 ml toluene and layering with 30 ml diethyl ether produced greenish blue crystals which were washed with 15 ml diethyl ether. Drying in vacuo resulted in 1.76 g (90%) of Co(N-MelM)₂(SPh)₂. IR 1575 (vs), 477 (s).

Analysis for C₂₇H₂₅N₄CoS₂
Calcd C 54.41 H 5.02 N 12.69 Co 13.35%, Found C 54.61 H 5.12 N 12.77 Co 12.24%.

Co(N-MelM)₂S₄ from Co(N-MelM)₂(SPh)₂

Solid 0.112 g sulfur (3.49 mmol) was added to a green solution of 0.311 g Co(N-MelM)₂(SPh)₂ (0.7 mmol) in 6 ml of N-Melm. The reaction mixture turned to brown in 2 min and was further stirred for 3 h. Addition of 50 ml THF resulted in the formation of brown microcrystalline solid. It was washed with 10 ml of toluene and then with 20 ml Et₂O and dried under vacuum to produce 0.2 g (89%) of Co(N-MelM)₂S₄. IR 1528 (vs), 466 (s).

Analysis for C₁₂H₁₂N₂CoS₄
Calcd C 27.34 H 3.44 N 15.94 Co 16.76%, Found C 28.28 H 3.65 N 14.97 Co 15.48%.

Crystallographic characterization of [Mn(N-MelM)₆]₂(S₂Ph)₂ and [Ni(N-MelM)₆]₂(S₂Ph)₂*

Light green crystals of [Mn(N-MelM)₆]₉(S₂Ph)₂ and blue-green crystals of [Ni(N-MelM)₆]₉(S₂Ph)₂ were obtained by layering their N-Melm solutions with ether and toluene respectively. The crystals were mounted on thin glass fibers using Paratone-N oil (Exxon) and epoxy, respectively. Unit cell parameters were obtained from the least squares fit of 25 reflections.

The space group P2₁/n (No. 14) was determined according to systematic absences and verified by successful refinement. Lorentz and polarization correction as well as numerical absorption correction was applied to the reflection intensities.

The structure of [Ni(N-MelM)₆]₉(S₂Ph)₂ was solved by direct methods (SHELXS-86) [10]. Correct positions for Ni, S, N and most of the C atoms were deduced from the electron density map. Subsequent least squares difference Fourier calculations (SHELX-76) [10] revealed positions for all non-hydrogen atoms. This set of atomic parameters was used as a starting set for the refinement of [Mn(N-MelM)₆]₉(S₂Ph)₂.

The structure of the Mn salt was refined with anisotropic thermal parameters for all non-hydrogen atoms while common thermal parameters were used for each type of hydrogen. In case of the Ni salt, where there was less data, the hydrogen atom positions were calculated for idealized distances (96 pm) and angles.

* Details of the crystallographic results have been deposited at the Cambridge Crystallographic Data Centre.
Table I. Selected bond distances [pm] and angles [°] in \([\text{M}(N\text{-MeIm})_6](S_2\text{Ph})_2\).

<table>
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<tr>
<th>Parameter</th>
<th>M = Mn</th>
<th>M = Ni</th>
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<tbody>
<tr>
<td>M – N1</td>
<td>224.8(2)</td>
<td>213.2(6)</td>
</tr>
<tr>
<td>M – N3</td>
<td>225.2(2)</td>
<td>212.5(6)</td>
</tr>
<tr>
<td>M – N5</td>
<td>229.0(2)</td>
<td>215.0(6)</td>
</tr>
<tr>
<td>N1 – M – N3</td>
<td>91.96(8); 88.04(8)</td>
<td>92.2(2); 87.8(2)</td>
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<tr>
<td>N1 – M – N5</td>
<td>88.26(8); 91.74(8)</td>
<td>88.1(2); 91.9(2)</td>
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<tr>
<td>N3 – M – N5</td>
<td>91.56(8); 88.44(8)</td>
<td>88.8(2); 91.2(2)</td>
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<tr>
<td>S1 – S2</td>
<td>202.2(1)</td>
<td>197.8(4)</td>
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<td>S1 – S2 – C13</td>
<td>108.1(1)</td>
<td>107.6(4)</td>
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Successful convergence was indicated by the maximum shift/error for the final refinement cycle. For both structures the highest peaks in the final difference maps were close to the S atoms. Details about data collection and refinement are given in Table II.

This research was supported by the U.S. National Science Foundation through CHE-92-12178. HK thanks “Studienstiftung des Deutschen Volkes” and BASF for a postdoctoral fellowship.

Table II. Data collection and refinement.

<table>
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<th><a href="S_2%5Ctext%7BPh%7D">\text{Mn}(N\text{-MeIm})_6</a>_2</th>
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<td>diff. Fourier map ([e^-/\text{Å}^3])</td>
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   b) E. Ramli, T. B. Rauchfuss, and C. L. Stern, J. Am. Chem. Soc. 112, 4043 (1990);
   c) S. Dev, E. Ramli, T. B. Rauchfuss, and S. R. Wilson, J. Am. Chem. Soc. 112, 6385 (1990);
   d) T. B. Rauchfuss, S. Dev, and S. R. Wilson, Inorg. Chem. 31, 153 (1992);
[5] [Ni(\text{N-MeIm})_6\text{(SPh)}_2] crystallizes in the triclinic space group P\overline{1} (C\overline{1}) with a = 7.495(1) Å, b = 10.932(4) Å, c = 12.237(3) Å, α = 106.61(2)°, β = 95.17(2)° and γ = 98.63(2)°, V = 940.4(9) Å³ (T = −75 °C).
[6] [Mn(\text{N-MeIm})_6\text{(SPh)}_2] crystallizes in the triclinic space group P\overline{1} (C\overline{1}) with a = 7.439(4) Å, b = 11.080(7) Å, c = 12.353(6) Å, α = 106.34(5)°, β = 94.67(4)° and γ = 97.97(5)°, V = 960(2) Å³ (T = −75 °C).