are complicated and will be the subject of a future report.

Acknowledgment. We thank the National Science Foundation for financial support.

Supplementary Material Available: Full tables of crystal parameters and results of data collection and refinement, bond distances, bond angles, and anisotropic displacement parameters for **2**, **4**, and **8** and a table of positional and thermal parameters and ORTEP drawings for **4** (35 pages); tables of observed and calculated structure factors (77 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of [M(*N*-methylimidazole)$_6$]S$_8$ (M = Mn, Fe, Ni, Mg). Polysulfide Salts Prepared by the Reaction *N*-Methylimidazole + Metal Powder + Sulfur

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Powdered magnesium, manganese, iron, and nickel were found to dissolve in *N*-methylimidazole (*N*-MeIm) solutions of elemental sulfur to give red-colored salts [M(*N*-MeIm)$_6$]S$_8$. The structure of the nickel complex was determined by single-crystal X-ray diffraction. The compound crystallizes in the triclinic space group $P\bar{1}$ with a = 8.027 (5) Å, b = 10.785 (2) Å, c = 11.531 (2) Å, α = 112.79 (2)°, β = 92.35 (3)°, γ = 96.11 (3)°, Z = 1. The structure analysis revealed a centrosymmetric cation that is analogous to other hexakis(imidazole) complexes. The compounds [M(*N*-MeIm)$_6$]S$_8$ are rare examples of polysulfide salts of transition-metal complexes. The IR spectra of the new compounds were analyzed by comparison with samples of [M(*N*-MeIm)$_6$]I$_2$ that were prepared by the reaction of the metal powders with iodine in *N*-MeIm solution.

Introduction

We have recently shown that donor solvents such as pyridine and *N*-alkylimidazoles promote the reaction of metal powders with elemental sulfur.[1] These reactions can be described using the notation L–M–X, where L is the donor ligand, M is a metal powder, and X is the oxidant. The L–M–X process can be viewed as a chemically well-behaved and synthetically useful form of oxidative corrosion.

Previous examples of L–M–X reactions are the syntheses of divalent acetonitrile complexes of the type [M(MeCN)$_6$](BF$_4$)$_2$ by the reaction of acetonitrile suspensions of metal powders with nitrosonium salts.[2-5] It has also been reported that several first-row transition metals dissolve in dimethyl sulfoxide (DMSO) solutions of sulfur dioxide to give salts of the type [M(DMSO)$_6$]X where X = SO_4^{2-} and $S_2O_7^{2-}$.[6] Manganese powder has long been known to react with an ether solution of iodine giving MnI$_2$.[7] Pohl and co-workers have synthesized salts of the anionic clusters $Fe_6S_6I_6^{2-}$ and $Fe_8S_6I_8^{2-}$ by the reaction I$^-$/Fe/S$_8$ + I$_2$, in weakly coordinating solvents.[8] The Lewis base in these processes is the iodide anion, and both sulfur and iodine serve as oxidants.

The reaction L/Cu/S$_8$ affords clusters of the type Cu$_4$(S$_5$)$_2$L$_4$ (L = *N*-MeIm and substituted pyridines) which, aside from their interesting structure, are noteworthy as intermediates in the conversion of copper metal to CuS. The L/Cu/S$_8$ reaction works for both pyridines and especially for *N*-alkylimidazoles, whereas the dissolution of zinc could only be effected in hot *N*-MeIm. The *N*-MeIm/Zn/S$_8$ and *N*-MeIm/Zn/Se$_n$ reactions afford tetrahedral coordination complexes of the type ZnS$_6$(*N*-MeIm)$_2$ and ZnSe$_4$(*N*-MeIm)$_2$.[9]

In this paper, we describe the products of the *N*-MeIm/M/S$_8$ reaction for M = Mn, Fe, Ni, and Mg. This investigation has resulted in the preparation of a series of polysulfide salts of metal complexes.

Results

Synthesis of [M(*N*-MeIm)$_6$]S$_8$. Suspensions of magnesium, manganese, iron, and nickel powders dissolve over a period of several days in a solution of elemental sulfur in *N*-MeIm. After a typical reaction period, the reaction mixtures consisted of a red precipitate and a red solution. The red precipitate proved to have the formula [M(*N*-MeIm)$_6$]S$_8$, and the red solution yielded the same product after layering with diethyl ether. For M = Mg, Mn, and Fe these reactions proceeded quantitatively at 80 °C in 1 h (eq 1). Nickel powder dissolves more slowly in the *N*-MeIm/S$_8$ solution, but the resulting red solution yielded [Ni(*N*-MeIm)$_6$]S$_8$ in 35% yield. The yield and rate of the nickel reaction can be increased by conducting the reaction at 50 °C, but the yields are not quantitative. Cobalt, chromium, vanadium, and titanium do not dissolve in *N*-MeIm/S$_8$ at room temperature even after several days. Cobalt metal reacts with *N*-MeIm solutions of elemental sulfur to give an insoluble solid that was not characterized. It was found that a suspension of sulfur in 33% aqueous ammonia was unreactive toward nickel powder. Solutions of sulfur in pyridine, acetonitrile, 3-methylpyrazole, *N*-methylmorpholine, ethylenediamine, and 2,2′-bipyridine/DMF were also found to be uneffective in this dissolving metal reaction. Moreover, small amounts of iodine did not accelerate the reactions nor did iodine induce the activation of chromium or cobalt.

$$\mathrm{M + S_8 + 6}N\text{-}\mathrm{MeIm} \rightarrow [\mathrm{M}(N\text{-}\mathrm{MeIm})_6]\mathrm{S_8} \qquad (1)$$

$$\mathrm{M = Mg, Mn, Fe, Ni}$$

The new compounds give highly conductive solutions in *N*-MeIm and the conductivities are comparable. They are soluble in DMF, but preliminary studies show that dissolution is accompanied by displacement of some of the *N*-MeIm ligands. For example, the manganese compound gives a turbid solution in

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Table I. Selected Bond Distances (Å) and Angles (deg) for the Cation in $[Ni(N\text{-MeIm})_6]S_8$

		Distances			
Ni–N1	2.117 (5)	N1–C2	1.327 (8)	C2–N3	1.324 (9)
N3–C4	1.354 (9)	N1–C5	1.365 (9)	C4–C5	1.362 (9)
N3–C6	1.467 (9)	Ni–N7	2.117 (5)	N7–C8	1.324 (8)
C8–N9	1.343 (8)	N9–C10	1.363 (9)	N4–C11	1.364 (8)
C10–C11	1.345 (9)	N9–C12	1.464 (9)	Ni–N13	2.125 (5)
N13–C14	1.329 (8)	C14–N15	1.360 (9)	N15–C16	1.363 (9)
N13–C17	1.383 (8)	C16–C17	1.34 (1)	N15–C18	1.467 (10)
		Angles			
N1–Ni–N1′	180.0	N1–Ni–N7	88.3 (2)	N1–Ni–N7′	91.7 (2)
N1–Ni–N13	89.0 (2)	N1–Ni–N13′	91.0 (2)	N7–Ni–N13′	88.8 (2)
N7–Ni–N7′	180.0	N7–Ni–N13	91.2 (2)	N13–Ni–N13′	180.0
Ni–N1–C2	128.7 (4)	Ni–N1–C5	127.0 (4)	Ni–N7–C8	127.0 (4)
Ni–N7–C11	127.7 (4)	C2–N1–C5	103.8 (5)	C8–N7–C11	105.3 (5)
Ni–N13–C14	126.5 (4)	Ni–N13–C17	128.2 (4)	C14–N13–C17	105.2 (5)

acetonitrile, possibly because of the precipitation of elemental sulfur. The nickel complex reacts with water to give black NiS.

Powdered samples of Mg, Mn, Fe, and Ni were also found to dissolve in an *N*-MeIm solution of iodine to give salts of the type $[M(N\text{-MeIm})_6]I_2$. Dissolution occurred in less than an hour for M = Mg, Mn, and Ni to give nearly colorless slurries. Iron dissolved very slowly at room temperature but quickly at 85 °C. Whereas cobalt powder did not give a soluble product with *N*-MeIm/S_8, it cleanly dissolved in hot *N*-MeIm/I_2 to give $[Co(N\text{-MeIm})_6]I_2$. The iodides were obtained as pale colored microcrystalline solids. These salts are poorly soluble in *N*-MeIm, but they are very soluble in acetonitrile and dimethylformamide.

Vibrational Spectroscopy. The IR spectra for $[M(N\text{-MeIm})_6]S_8$ are quite similar for M = Mg, Mn, Fe, and Ni. In general, the spectral features can be classified as cation and anion modes based on the disparate masses of the constituent bonded atoms. The ν_{SS} bands for polysulfide anions have been shown to occur in the region 550 – 420 cm^{-1}.[10] The three IR bands for the anion in $[M(N\text{-MeIm})_6]S_8$ (Figure 1) were observed at ~524, ~508, and ~444 cm^{-1}. Above 550 cm^{-1}, the spectra of $[M(N\text{-MeIm})_6]S_8$ are dominated by bands associated with $[M(N\text{-MeIm})_6]^{2+}$, which largely correspond to absorptions observed for free *N*-MeIm. Furthermore, IR spectra in the range >550 cm^{-1} are virtually identical for the iodide and octasulfide salts. Samples of $[M(N\text{-MeIm})_6]I_2$ did not show any absorption bands in the 550–400-cm^{-1} region.

Crystallographic Studies. $[Ni(N\text{-MeIm})_6]S_8$ and $[Mn(N\text{-MeIm})_6]S_8$ crystallize in the same space group with very similar cell dimensions. The three-dimensional structure was solved for the nickel complex. The lattice consists of isolated $[Ni(N\text{-MeIm})_6]^{2+}$ and S_8^{2-} subunits. The cation is crystallographically centrosymmetric (Figure 2). The Ni–N distances and N–Ni–N angles are unexceptional (Table I), and the structure resembles other $[Ni(imidazole)_6]X_2$ salts where X = NO_3 and BF_4.[11-15]

Detailed discussion of the S_8^{2-} dianion is limited by a disorder problem arising from a pseudocenter of symmetry. The thermal parameters indicate that the positions of S2 and S7 are poorly defined, and the angles and distances associated with these atoms are not considered to be reliable (Table II). The conformation of the central five sulfur atoms of the S_8^{2-} anion is very similar to those of salts of S_7^{2-} [16-18] and S_6^{2-}.[19-21] Differences are observed in the orientations of the terminal atoms of the chains. However the conformation of our salt of S_8^{2-} differs substantially from that

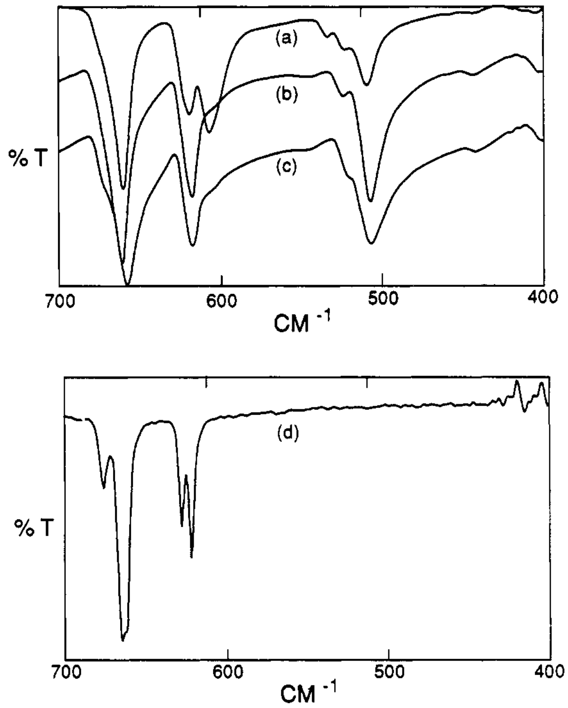

Figure 1. IR spectra (700–400 cm^{-1}) for $[Ni(N\text{-MeIm})_6]S_8$ (a), $[Fe(N\text{-MeIm})_6)]S_8$ (b), $[Mn(N\text{-MeIm})_6)]S_8$ (c), and $[Ni(N\text{-MeIm})_6]I_2$ (d).

Table II. Distances (Å) and Angles (deg) for the Anion in $[Ni(N\text{-MeIm})_6]S_8$

S1–S2[a]	2.104 (9)	S2–S3	2.191 (9)
S3–S4	2.055 (8)	S4–S5	2.045 (7)
S5–S6	2.060 (7)	S6–S7	2.026 (9)
S7–S8[a]	2.099 (8)	S1–S2–S3	106.0 (4)
S2–S–S4	113.6 (4)	S3–S4–S5	108.3 (3)
S4–S5–S6	108.6 (3)	S5–S6–S7	107.2 (3)
S6–S7–S8	111.9 (3)	S1–S2–S3–S4	90.3 (4)
S2–S3–S4–S5	100.4 (4)	S3–S4–S5–S6	−83.9 (4)
S4–S5–S6–S7	−84.9 (4)	S5–S6–S7–S8	91.1 (4)

[a] The bond lengths S1–S2 and S7–S8 were constrained to be equivalent ±0.005 Å preceding each least-squares refinement cycle.

Table III. Cell Parameters (−75 °C) for $[M(N\text{-MeIm})_6]S_8$ (M = Mn, Ni)

$[Mn(N\text{-MeIm})_6]S_8$	$[Ni(N\text{-MeIm})_6]S_8$
a = 7.986 (11) Å	a = 8.027 (5) Å
b = 11.043 (4) Å	b = 10.785 (2) Å
c = 11.517 (5) Å	c = 11.531 (2) Å
α = 112.38 (3)°	α = 112.79 (2)°
β = 92.82 (7)°	β = 92.35 (2)°
γ = 95.01 (7)°	γ = 96.11 (3)°
V = 932 (3) $Å^3$	V = 911.4 (7) $Å^3$

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Table IV. Selected Physical Properties of the First-Row Transition Metals

metals	cryst struct	heat of vaporization, kcal/mol	std redn potential, V	first ionization energy, eV	work function, eV	hardness, Mohs' scale
Ti	hcp	101.63	-1.63	6.83	4.33	5.5
V	bcc	106.77	-1.2	6.74	4.3	5.0
Cr	bcc	81.14	-0.557	6.76	4.5	9.0
Mn[a]	bcc	52.52	-1.029	7.43	4.1	5.0
Fe[a]	bcc	83.68	-0.409	7.90	4.5	4.5
Co	hcp	89.22	-0.28	7.86	5.0	5.5
Ni[a]	fcc	89.60	-0.23	7.63	5.15	3.5
Cu[a]	fcc	72.74	-0.340	7.72	4.65	2.5
Zn[a]	hcp	27.62	-0.763	9.39	4.3	2.5

[a] These metals dissolve in *N*-methylimidazole solutions of sulfur.

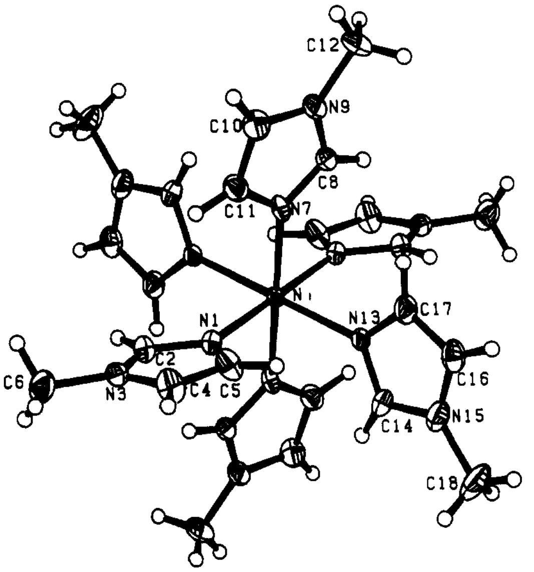

Figure 2. Structure of the cation in the salt $[Ni(N\text{-}MeIm)_6]S_8$ with thermal ellipsoids drawn at the 35% probability level.

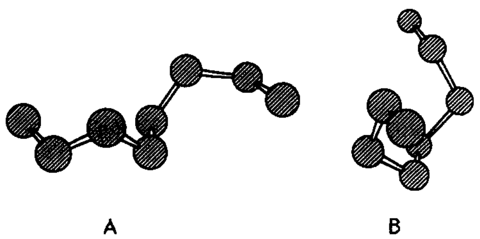

Figure 3. Structures of the octasulfido anions in $[Ni(N\text{-}MeIm)_6]S_8$ (A) and $(NHEt_3)_2S_8$ (B).

found in $(NEt_3H)_2S_8$,[22] the only other crystallographically characterized octasulfide salt (Figure 3).[23] The conformation of the latter species may be a consequence of hydrogen bonding between the N*H* and the terminal atoms of the polysulfides.

Optical Spectroscopy. All of the new compounds form red crystals that dissolve in *N*-MeIm to give red solutions when concentrated, as observed under synthesis conditions. However solutions of these $[M(N\text{-}MeIm)_6]S_8$ compounds are blue-green when dilute ($\sim 10^{-3}$ M) with a strong absorption at 618 nm (Figure 4). The optical spectra of 10^{-3} M solutions of $[Mn(N\text{-}MeIm)_6]S_8$ and $(PPh_4)_2S_6$ in *N*-MeIm are virtually identical. Furthermore, we found that the optical spectrum of a 10^{-3} M *N*-MeIm solution of $(PPh_4)_2S_6$ did not change upon the addition of 0.25 equiv of S_8; this shows that the chromophore has the stoichiometry $[S_x^-]_n$, where $x \leq 3$. This in turn is consistent with S_3^- as the chromophore.

Magnetism. The magnetic properties of the Mn, Fe, and Ni salts were measured over the temperature range 5–300 K by using a magnetic field of 10 kG. Both $1/\chi$ and μ are linearly dependent on temperature. The Mn and Ni salts show a Curie behavior as their magnetic susceptibilities are linearly dependant on $1/T$. The Fe salt follows the Curie–Weiss law with $\Theta = -6$ K indicative of small antiferromagnetic exchange. The magnetic moments at 300 K are 5.9, 5.4, and 2.7 μ_B for the Mn, Fe and Ni salts respectively; these values are in the range expected for high-spin complexes $[M(imidazole)_6](ClO_4)_2$ where M = Mn^{2+}, Fe^{2+}, and Ni^{2+}, as discussed earlier by Reedijk and others.[24-26]

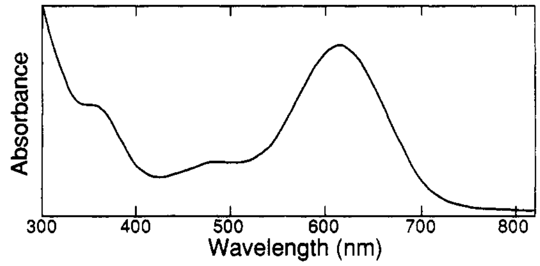

Figure 4. Optical spectrum of a 0.001 M *N*-MeIm solution of $[Mn(N\text{-}MeIm)_6]S_8$.

Discussion

As indicated in the review by Sunberg and Martin, imidazole is a particularly effective ligand for transition metal ions.[27] It is 79 times more basic than pyridine yet it exhibits the π-acceptor properties lacking in ammonia. The small C–N–C angle of 108° facilitates the formation of hexakis(imidazole) complexes. The C–N–C angle in pyridine is 116°50′, which leads to serious interligand steric repulsions in $[M(py)_6]^z$ complexes.[28]

Manganese, iron, nickel, and magnesium dissolve in a solution of sulfur in *N*-methylimidazole giving the isostructural compounds $[M(N\text{-}MeIm)_6]S_8$. Two general mechanisms can be considered for these dissolving-metal syntheses. One mechanism entails the initial formation of sulfido species on the metal surface. This is followed by solubilization by the complexing action of the donor solvent, possibly in conjunction with added sulfur. This model emphasizes the direct attack of sulfur on the metal surface and is related to the phenomenon of tarnishing. This pathway may describe the $N\text{-}MeIm/Cu/S_8$ reaction since both Cu_2S and Cu metal serve equally well in the synthesis of $Cu_4(S_5)_2(N\text{-}MeIm)_4$.[29] The oxidative addition of sulfur to low-valent metal complexes[30] is a good model for the initial stage envisioned for this mechanism.

Our results are related to observations made in studies on the sulfur sodium battery. This battery utilizes the sodium + sulfur/sodium polysulfide couple and operates at elevated temperatures. In several designs of this cell, one of the current collectors

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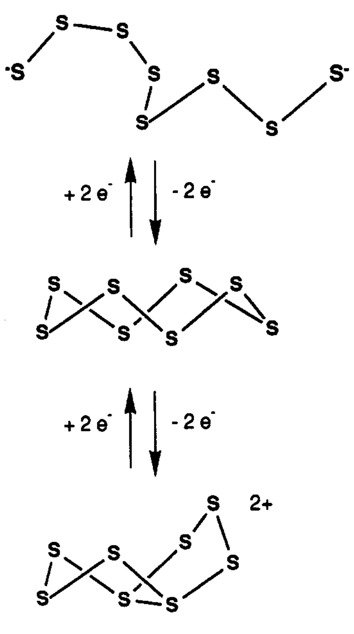
Scheme I



is the metal container for the polysulfide melt. Manganese, iron, and nickel were found to be unsuitable container materials because of their solubility in the sodium polysulfide melts.[31]

A second mechanistic possibility for $L/M/S_8$ reactions emphasizes the association of the donor solvent with the metal surface. In view of the strong donor properties of imidazoles, its presence renders metals substantially more reducing. However this thermodynamic effect apparently does not determine the ability of N-MeIm/S_8 to dissolve metals since there is no correlation with redox potentials. Several characteristic properties of the transition metals are presented in Table IV.[32] No single property appears to correlate with the reactivity of the metals toward N-MeIm solutions of elemental sulfur.[1,9]

There have been many studies on the structural chemistry of polysulfide anions, but salts of S_8^{2-} have only been recently reported. The octasulfido dianion is of special significance as it is the product of the 2e⁻ reduction of S_8. Together with the 2e⁻ oxidation of S_8,[33] one can depict the redox relationships shown in Scheme I. We do not attach mechanistic significance to the presence of the octasulfido anion since polysulfido compounds are kinetically labile and the octasulfide dianion must be assumed to result from stabilization provided by the lattice. Furthermore, our spectroscopic studies on N-MeIm solutions of $[M(N\text{-MeIm})_6]S_8$ indicate the dynamic equilibria shown in eqs 2 and 3. The electrochemical reduction of S_8 proceeds by the initial

$$S_8^{2-} \rightleftarrows 2S_3^- + \tfrac{1}{4}S_8 \tag{2}$$

$$S_6^{2-} \rightleftarrows 2S_3^- \tag{3}$$

formation of S_8^{2-} followed by a slower conversion to S_6^{2-} and elemental sulfur.[34-36] In acetonitrile, this reduction occurs at −1.4 V vs Ag/AgCl and further reduction (to S_4^{2-}) occurs at −1.8 V. The behavior described by eq 3 has been established through studies on $(NBu_4)_2S_6$.[19]

Table V. X-ray Crystallographic Data for $[Ni(N\text{-MeIm})_6]S_8$ (See Table III for Unit Cell Data)

formula	$C_{24}H_{36}N_{12}NiS_8$
fw	807.85
Z	1
cryst syst	triclinic
space group	$P\bar{1}$
ρ_{calcd}, g cm^{-3}	1.472
color, habit	orange-red, columnar
{forms} size, mm	{001} 0.03; {010} 0.07; {100} 0.22
T, K	198
μ(Mo, Kα), cm^{-1}	10.10
diffractometer	Enraf-Nonius CAD4
transm factor range	0.945–0.857 (numerical)
2θ limit, deg (octants)	48.0 ($-h,\pm k,\pm l$)
radiation	Mo Kα (λ = 0.71073 Å)
monochromator	graphite
no. of reflcns collcd (unique, R_i)	3165 (2849, 0.025)
no. of reflcns obsd ($I > 2.58\sigma(I)$)	1628
R	0.063
R_w	0.073 (p = 0.03)
density range in final ΔF map, e/Å^3	−0.45 to +1.68 (near S2, S7)

Table VI. Atomic Coordinates for Non-Hydrogen Atoms in $[Ni(N\text{-MeIm})_6]S_8$[a]

	x/a	y/b	z/c
Ni	0.0	0.0	0.0
N1	0.1174 (7)	−0.1780 (5)	−0.0743 (5)
C2	0.0735 (8)	−0.2979 (6)	−0.0693 (6)
N3	0.1871 (7)	−0.3814 (5)	−0.1122 (5)
C4	0.3136 (8)	−0.3152 (7)	−0.1488 (7)
C5	0.2694 (8)	−0.1895 (7)	−0.1237 (7)
C6	0.1809 (10)	−0.5196 (7)	−0.1167 (7)
N7	0.1882 (6)	0.0761 (5)	0.1535 (5)
C8	0.2307 (8)	0.2042 (6)	0.2322 (6)
N9	0.3534 (7)	0.2162 (6)	0.3202 (5)
C10	0.3914 (8)	0.0887 (7)	0.2955 (7)
C11	0.2892 (8)	0.0041 (7)	0.1940 (7)
C12	0.4358 (9)	0.3427 (7)	0.4192 (7)
N13	0.1501 (7)	0.0841 (5)	−0.1060 (5)
C14	0.1227 (8)	0.0580 (7)	−0.2282 (6)
N15	0.2509 (8)	0.1218 (6)	−0.2665 (6)
C16	0.3621 (8)	0.1935 (7)	−0.1637 (7)
C17	0.3003 (8)	0.1701 (7)	−0.0663 (7)
C18	0.2634 (10)	0.1156 (8)	−0.3952 (7)
S1	0.3208 (8)	0.5706 (6)	0.2337 (7)
S2	0.2208 (9)	0.7325 (7)	0.3698 (6)
S3	0.0003 (8)	0.6410 (6)	0.4283 (6)
S4	0.0545 (6)	0.5911 (5)	0.5793 (4)
S5	0.0685 (6)	0.3874 (6)	0.5124 (5)
S6	−0.1712 (6)	0.2859 (5)	0.4870 (5)
S7	−0.2261 (7)	0.2822 (6)	0.6556 (8)
S8	−0.3436 (8)	0.4497 (5)	0.7630 (6)

[a] Inversion symmetry was imposed on the $Ni(N\text{-MeIm})_6^{2+}$ cation and the disordered S_8^{2-} anion.

Summary

N-Methylimidazole solutions of sulfur dissolve several transition metals to give polysulfide salts of hexakis(N-MeIm) complexes. These polysulfide salts are significant because they represent isolable intermediates in the formation of polysulfide complexes.[29] The stabilization arises because of the strong donor properties of N-MeIm and the relatively low basicity of S_8^{2-}. Complementary to the use of L–M–X methods described in this paper is our finding that under certain circumstances metal sulfides as well as metal carbonyls are reactive toward N-MeIm solutions of elemental sulfur.

Experimental Section

Materials. All manipulations were carried out under an atmosphere of purified nitrogen by using standard Schlenk techniques. N-Methylimidazole (Aldrich, 99%) was distilled under reduced pressure (35–45

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Table VII. Thermal Parameters for the Octasulfide Anion in $[Ni(N\text{-}MeIm)_6]S_8$[a]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	0.051 (1)	−0.067 (1)	0.072 (1)	0.039 (1)	0.016 (1)	−0.004 (1)
S2	0.127 (1)	0.113 (1)	0.086 (1)	0.054 (1)	−0.046 (1)	−0.049 (1)
S3	0.075 (1)	0.119 (1)	0.094 (1)	0.068 (1)	0.000 (1)	0.016 (1)
S4	0.060 (1)	0.065 (1)	0.044 (1)	0.012 (1)	0.008 (1)	0.005 (1)
S5	0.052 (1)	0.086 (1)	0.083 (1)	0.036 (1)	0.035 (1)	0.032 (1)
S6	0.062 (1)	0.070 (1)	0.051 (1)	0.011 (1)	0.010 (1)	0.006 (1)
S7	0.044 (1)	0.039 (1)	0.179 (1)	0.029 (1)	0.024 (1)	0.014 (1)
S8	0.072 (1)	0.039 (1)	0.050 (1)	0.025 (1)	0.001 (1)	0.005 (1)

[a] Temperature factors: anisotropic, $\exp\{-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2b^*c^*U_{23}kl + 2a^*c^*U_{13}hl + 2a^*b^*U_{12}hk)\}$.

°C, 0.1 mmHg) from barium oxide and was stored under nitrogen. The following elements were used: Mg powder (Alfa, 325 mesh, 99%), Mn powder (Alfa, 325 mesh, 99.9%), Fe powder (Cerac, 325 mesh, 99.9%), Ni powder (Aldrich, 100 mesh, 99%), and sulfur powder (EM Science, 99%). The following instruments were employed: Perkin-Elmer Model 1750 FTIR, Hewlett-Packard Model 8452A UV-vis spectrophotometer, and Quantum Design SQUID magnetometer.

Solution conductivities were measured with a YSI Incorporated Model 31A conductivity bridge. These measurements were performed under an inert atmosphere by using Schlenk techniques. A calculated amount of the compound was added to 20 mL of *N*-MeIm, and the conductance of the resulting solution was recorded and compared with a blank. The difference between the solution and the blank is the conductance of the complex, *L*; the molar conductance was calculated by using the relation

$$\Lambda_M = 1000L/C_M$$

where C_M is the concentration, typically 4.35×10^{-4} M. The molar conductance of a 0.00235 M solution of S_8 in *N*-MeIm was 5.49 Ω^{-1} cm^{-2} mol^{-1}.

Microanalyses were performed by the School of Chemical Sciences Microanalytical Laboratory. Metals and sulfur were analyzed by the inductively coupled plasma technique utilizing a Perkin-Elmer Plasma II argon ion instrument.

$[Ni(N\text{-}MeIm)_6]S_8$. To a mixture of 1.578 g of sulfur (6.15 mmol) in 20 mL of *N*-MeIm was added 0.358 g of nickel powder (6.10 mmol). The resulting solution was stirred at ambient temperature over the course of 10–14 days. The resulting dark red color solution was filtered to remove undissolved nickel and sulfur. Addition of 50 mL of Et_2O to the filtrate gave a bright red precipitate, which was washed with 3 × 10 mL of Et_2O and dried under high vacuum. The same reaction can be completed in less than 1 day at 50–60 °C. Yield: 1.72 g (35 %). Anal. Calcd for $C_{24}H_{36}N_{12}NiS_8$: C, 35.68; H, 4.49; N, 20.79; Ni, 7.26; S, 31.75. Found: C, 35.25; H, 4.40; N, 20.66; Ni, 7.26; S, 31.29. Λ_M = 66.44 Ω^{-1} cm^{-2} mol^{-1} (4.43×10^{-4} M in *N*-MeIm), 144 Ω^{-1} cm^{-2} mol^{-1} (4.43×10^{-4} M in DMF).

$[Mg(N\text{-}MeIm)_6]S_8$. This procedure was adapted from the procedure for the corresponding nickel complex. Treatment of 0.167 g of Mg (6.88 mmol), 1.801 g of sulfur (7.02 mmol), and 30 mL of *N*-MeIm at 95 °C for 12 h gave a red solution. Layering of this solution with toluene gave 4.75 g (90%) of red microcrystalline product. Anal. Calcd for $C_{24}H_{36}N_{12}MgS_8$: C, 37.27; H, 4.69; N, 21.72; Mg, 3.14; S, 33.17. Found: C, 37.20; H, 4.74 N, 21.77; Mg, 3.29; S, 33.33. Λ_M = 62.55 Ω^{-1} cm^{-2} mol^{-1} (4.33×10^{-4} M in *N*-MeIm).

$[Fe(N\text{-}MeIm)_6]S_8$. To a mixture of 0.329 g of iron (5.89 mmol) and 1.511 g of sulfur (5.89 mmol) powders was added 20 mL of *N*-MeIm. The resulting slurry was stirred, and the progress of the reaction was monitored visually by checking for the presence of iron powder adhering to the magnetic stir bar. The reaction was allowed to proceed until all of the metal had dissolved, giving a homogeneous red solution and a red powder. Typically reactions were complete after 10–14 days. The red supernatant was decanted and layered with 70 mL of Et_2O to give dark red microcrystals. The red precipitate was washed with 50 mL of diethyl ether and dried under reduced pressure at room temperature. Yield: 4.69 g (96%). The same reaction can be completed in 2 h at 80 °C. Anal. Calcd for $C_{24}H_{36}N_{12}FeS_8$: C, 35.80; H, 4.52; N, 20.88; Fe, 6.94; S, 31.86. Found (microcrystals, red precipitate): C, 35.82, 35.48; H, 4.52, 4.83; N, 20.89, 20.89; Fe, 6.95, 7.19. Λ_M = 60.59 Ω^{-1} cm^{-2} mol^{-1} (4.34×10^{-4} M in *N*-MeIm).

$[Mn(N\text{-}MeIm)_6]S_8$. To a mixture of 0.320 g of manganese (5.82 mmol) and 1.494 g of sulfur (5.83 mmol) powders was added 20 mL of *N*-methylimidazole. The resulting slurry was stirred for 9 days, giving a red solution and red precipitate. After the solution was decanted and layered with 70 mL of diethyl ether, large red crystals were obtained (the largest was ~20 × 1 × 1 mm). The combined solid products were washed with 50 mL of Et_2O and dried under reduced pressure. Yield: 4.4 g (95%). The same reaction is complete in 12 h at 90 °C. Anal. Calcd for $C_{24}H_{36}N_{12}MnS_8$: C, 35.84; H, 4.52; N, 20.91; Mn, 6.83. Found (crystals, red precipitate): C, 35.86, 34.71; H, 4.52, 4.41; N, 20.06, 20.48; Mn, 6.90, 7.09. Λ_M = 50.57 Ω^{-1} cm^{-2} mol^{-1} (4.35×10^{-4} M in *N*-MeIm).

$[Ni(N\text{-}MeIm)_6]I_2$. To a mixture of 0.340 g of nickel powder (5.79 mmol) and 1.50 g of I_2 (5.91 mmol) was added 15 mL of *N*-MeIm. The reaction was exothermic, and within 30 min all of the nickel had dissolved. The reaction mixture was allowed to stir for 12 h, giving a purple slurry. Addition of 20 mL of Et_2O followed by filtration gave pale violet microcrystals. Yield: 5.64 g (97%). Anal. Calcd for $C_{24}H_{36}N_{12}I_2Ni$: C, 35.80; H, 4.48; N, 20.79. Found: C, 35.63; H, 4.50; N, 20.86.

$[Mg(N\text{-}MeIm)_6]I_2$. The procedure is similar to that employed for the corresponding nickel diiodide complex. The reaction of 2.35 g of I_2 (9.262 mmol), 0.224 g of Mg (9.21 mmol), and 25 mL of *N*-MeIm gave 8.72 g (98%) of white microcrystals. Anal. Calcd for $C_{24}H_{36}N_{12}I_2Mg$: C, 37.40; H, 4.71; N, 21.80; I, 32.93; Mg, 3.15. Found: C, 36.79; H, 4.65; N, 21.02; I, 33.02; Mg, 3.62.

$[Mn(N\text{-}MeIm)_6]I_2$. The procedure is similar to that employed for the corresponding nickel diiodide complex. Treatment of 0.462 g of manganese (8.41 mmol) with 2.145 g of I_2 (8.45 mmol) in 25 mL of *N*-MeIm gave 8.23 g (98%) of a pale violet microcrystalline solid. Anal. Calcd for $C_{24}H_{36}N_{12}I_2Mn$: C, 35.97; H, 4.53; N, 20.97; I, 31.67; Mn, 6.86. Found: C, 36.27; H, 4.58; N, 21.15; I, 30.81; Mn, 7.29.

$[Fe(N\text{-}MeIm)_6]I_2$. The procedure is similar to that employed for the corresponding nickel diiodide complex except that no reaction was evident at room temperature. The reaction was conducted at 85 °C for 12 h. The treatment of 2.323 g of I_2 (9.15 mmol) with 0.502 g of Fe (8.99 mmol) in 25 mL of *N*-MeIm gave 8.10 g (90%) of pale violet microcrystals. Anal. Calcd for $C_{24}H_{36}N_{12}FeI_2$: C, 35.93; H, 4.52; N, 20.94; Fe, 6.96; I, 31.64. Found: C, 35.88; H, 4.51; N, 20.94; Fe, 7.12; I, 31.58.

$[Co(N\text{-}MeIm)_6]I_2$. The procedure is similar to that employed for the corresponding iron diiodide complex. The addition of 0.248 g of Co (4.21 mmol) and 1.08 g of I_2 (4.26 mmol) in 16 mL of *N*-MeIm at 110 °C for 12 h gave 3.31 g (98%) of pale brown microcrystals. Anal. Calcd for $C_{24}H_{36}N_{12}CoI_2$: C, 35.80; H, 4.51; N, 20.86; Co, 7.32; I, 31.52. Found: C, 35.94; H, 4.61; N, 20.90; Co, 6.77; I, 31.84.

Magnetic Susceptibility Measurements. For magnetic susceptibility measurements, weighed samples were loaded into gelatine capsules in powder form inside a nitrogen drybox. An empty gelatine capsule, which served as a blank, was also weighed in an inert-atmosphere box. $\chi_{paramagnetic}$ was calculated as follows:[37]

$$\chi_{paramagnetic} = \chi_{measured} - \chi_{diamagnetic}$$

$\chi_{diamagnetic}$ was calculated for *N*-methylimidazole by using Pascal's constants as listed in ref 37. $\mu_{eff.}$ was calculated by using the formula

$$\mu_{eff} = 2.828(\chi T)^{1/2}$$

X-ray Crystallographic Studies. Crystals of $[M(N\text{-}MeIm)_6]S_8$ (M = Mn, Ni) were prepared by solvent layering methods using *N*-methylimidazole and diethyl ether. Selected bond distances and angles and relevant data are listed in Tables I and II. Cell parameters for $[M(N\text{-}MeIm)_6]S_8$ (M = Mn, Ni) are listed in Table III. Assuming simple octahedral geometry, a 0.02-Å increase in metal–nitrogen bond length for the manganese complex should increase the volume of the $[M(N\text{-}MeIm)_6]^{2+}$ ion by 1.03%. The experimental increase in cell volume was 1.02%.

The structure of $[Ni(N\text{-}MeIm)_6]S_8$ was solved by Patterson methods (SHELXS-86[38]); the nickel position was deduced from a vector map and

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partial structure expansion gave postions for the *N*-MeIm ligands. Subsequent least-squares refinement (SHELXS-76)[39,40] and difference Fourier syntheses revealed positions for the disordered sulfur atoms. Hydrogen atoms were included as fixed contributors in idealized positions. In the final cycle of least squares, anisotropic thermal coefficients were refined for non-hydrogen atoms and a common isotropic thermal parameter was varied for hydrogen atoms. Owing to the high correlation coefficients (see supplementary material), the S1–S2 and S7–S8 bond lengths were constrained to a free variable (±0.005 Å) preceding each refinement cycle. Successful convergence was indicated by the maximum shift/error (0.07) for the final cycle. The highest peaks in the final difference Fourier map were in the vicinity of the disordered atom S7 (and consequently S2). A final analysis of variance between observed and calculated structure factors showed no apparent systematic errors with respect to Miller index, sin θ, or amplitude.

Refinement of an ordered model in the acentric space group converged with non-positive-definite thermal coefficients, unreasonable bond length ranges (Ni–N, 2.01–2.25 Å, and S–S, 1.87–2.34 Å), distorted imidazole ring geometries, greater residual electron density, and higher agreement factors. Refinement with no constraints in the centric space group converged with nonsensical thermal coefficients for S7. A subsequent Fourier synthesis located maximum residual electron density in the vicinity of atom S7 (and S2). Attempts to refine a more complex model with additional disorder for site S7 were not successful.

Details on the data collection are presented in Table V while atomic coordinates and thermal parameters are listed in Tables VI and VII.

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Supplementary Material Available: Plots of magnetism data, an ORTEP diagram of the disordered S_8^{2-} anion, and tables of thermal parameters, bond distances and angles, and hydrogen atom positions (8 pages); a structure factor table (11 pages). Ordering information is given on any current masthead page.

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Polydentate Ligands Containing Phosphorus. 13. Synthesis and Molecular Structure of (Tri-*n*-butylphosphine)[tris(diphenylthiophosphinoyl)methanido]silver(I), $(n\text{-Bu})_3PAg\{[(S)PPh_2]_3C\}$[1]

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The synthesis, NMR spectra, and molecular structure are described for (tri-*n*-butylphosphine)[tris(diphenylthiophosphinoyl)methanido]silver(I). The compound crystallizes in monoclinic space group $P2_1/c$, with a = 18.192 (3) Å, b = 12.986 (2) Å, c = 21.194 (5) Å, β = 109.42 (1)°, and Z = 4. The molecule possesses pseudotetrahedral geometry about silver with the anionic ligand bonded via the three sulfur atoms in a tripodal, tridentate fashion with an average Ag–S bond length of 2.63 Å. The Ag–P (tri-*n*-butylphosphine) bond length is 2.402 (3) Å. The ^{31}P NMR spectrum at ambient temperature indicates $^1J(^{107}Ag-^{31}P)$ and $^1J(^{109}Ag-^{31}P)$ of 488.3 and 564.0 Hz, respectively, as well as $^3J(^{31}P-^{31}P)$ of 7.3 Hz.

Introduction

Tris(diphenylthiophosphinoyl)methanide, $\{[Ph_2P(S)]_3C\}^-$ (**1**), is the prototype of a recently discovered series of uninegative ligands[1a,3-6] that are related to **1** via replacement of the phenyl groups by other organic groups such as methyl[5,7-9] or replacement of one or more sulfur atoms by other chalcogens such as oxygen or selenium.[1a,6,10] These ligands can bond in a tridentate manner as has been shown in the case of a mercury(II) complex, $\{[Ph_2P(S)][Me_2P(S)]_2C\}HgCl$,[5,7] of the tetramethyl analogue of **1** or in a bidentate mode as in a platinum(II) complex, $Et_3PPtCl\{[(S)PPh_2]_3C\}$,[11] of **1** and in scandium, yttrium, and lutetium complexes, $M\{[(O)PPh_2]_3C\}_3$,[12] of the trioxide analogue of **1**.

This paper describes a convenient general method for the synthesis of complexes of this type of ligand as exemplified by the first silver complex, $(n\text{-Bu})_3PAg\{[(S)PPh_2]_3C\}$ (**2**),[1b,c] containing the trisulfide ligand **1**. Also reported are the molecular structure and multinuclear NMR data for **2**. This is the first crystal structure reported in which **1** behaves as a tripodal ligand.

Experimental Section

$[(n\text{-Bu})_4N]\{[Ph_2P(S)]_3C\}$ was prepared as described earlier.[4,6] $(n\text{-Bu})_3P$ was obtained from Strem Chemicals, Inc., and distilled before use. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN.

Synthesis of $(n\text{-Bu})_3PAg\{[(S)PPh_2]_3C\}$ (2). To a mixture of 0.90 g (1.0 mmol) of $[(n\text{-Bu})_4N]\{[Ph_2P(S)]_3C\}$ and 0.20 g (1.0 mmol) of (*n*-

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