Several lines of evidence point to the fact that both **2** and **3b** have a common structure in solution, i.e. **2** apparently dissociates to give a monomeric species that is identical with **3**. Thus, dissolution of **2** and **3b** results in identical UV–vis and "reversed axial" frozen-solution EPR spectra (see Experimental Section). Copper(II) complexes in TBP geometry with tripodal ligands normally display a "reversed axial" pattern in the frozen-solution EPR spectra with $g_\parallel < 2.0$.[6d,15] The conclusion is also supported by the measured molar conductivities of **2** and **3b**, which are within the range expected for 1:1 electrolytes.[16]

This mononuclear fluorocopper(II) complex could also be generated by using added fluoride in the form of tetrabutylammonium fluoride (Bu4NF). For these experiments an aqua complex $[Cu^{II}(TMPA)H_2O](ClO_4)_2$ (**4**) was utilized since the water in **4** can be easily replaced and the perchlorate counteranions present cannot serve as a F⁻ source. Thus, Bu4NF was added to complex **4** and the reaction was followed by EPR and UV–vis spectroscopy as illustrated in Figure 4. EPR spectrum 1 corresponds to a solution of the aqua complex, $[Cu^{II}(TMPA)H_2O](ClO_4)_2$ (**4**), in a 4:1 mixture of EtOH–MeOH (77 K). Addition of 5 equiv of Bu4NF·3H2O to the solution of **4** results in a well-resolved EPR spectral pattern (spectrum 3), essentially

identical with that of a solution of **3b** (spectrum 2) under the same conditions. The electronic spectra of **3b** and **4** + 5Bu4NF·3H2O are also identical (insets, Figure 4) and different from that of **4**, strongly suggesting that F⁻ has displaced the aqua ligand in **4** to give a fluoride complex that has solution properties substantially the same as **3b**.

In summary, fluoride–Cu(II) complexes with the tripodal tetradentate ligand TMPA form when the corresponding [Cu^{I}-(TMPA)CH3CN]PF6 complex is reacted with dioxygen. Interesting mono- and dinuclear structures form, demonstrating the flexibility of the TMPA ligand in forming Cu(II) complexes in several coordination geometries (i.e. trigonal bipyramidal and pseudooctahedral) and demonstrating that F⁻ may serve either as a terminal or bridging ligand in these systems. Further examination of these and other compounds may assist in further understanding the ligating properties of fluoride ion with copper ion complexes and metalloproteins.

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Preparation and X-ray Structure of Tetraphenylphosphonium Amminebis(tetrasulfido)nitrosylruthenate, (PPh4)[Ru(NO)(NH3)(S4)2]: The First Polysulfido Nitrosyl Complex of Ruthenium

A. Müller,* M. Ishaque Khan,† E. Krickemeyer, and H. Bögge

(PPh4)[Ru(NO)(NH3)(S4)2] has been prepared by reacting trichloronitrosylruthenium with a solution of tetraphenylphosphonium polysulfide in ammoniacal acetonitrile and characterized by X-ray crystallography. Crystal data at 21 °C: dark red-brown crystals, monoclinic space group $P2_1/n$, $a = 11.341$ (3) Å, $b = 13.091$ (3) Å, $c = 20.829$ (5) Å, $\beta = 104.93$ (2)°, $V = 2987.8$ Å³, $Z = 4$; the structure was refined to $R = 0.046$ and $R_w = 0.043$ for 4986 unique reflections. Ru–N(NO), Ru–N(NH3), and Ru–S distances are 1.717 (4), 2.146 (4), and 2.394 (1)–2.408 (1) Å, respectively. The Ru–NO moiety is approximately linear, with an Ru–N–O angle of 175.7 (3)°.

Introduction

(Polysulfido)metal complexes are of current interest.[1,2] Studies in this area have been further motivated due to evidence of the significant roles played by metal sulfide species in some vital industrial[3] (e.g. fuel processing/hydrodesulfurization catalysis[1,2]) and biological[4] (e.g. electron transfer and nitrogen fixation) processes.

Consequently, a sizable literature on syntheses, characterization, and reactivities of these complexes, some of which have been characterized by X-ray crystallography, is now available.[1] There appears to be, however, a striking paucity of the similar complexes of ruthenium, and only few polysulfido complexes of the latter have been reported,[5] despite the fact that a number of complexes exist with monodentate and/or polydentate ligands bonded to ruthenium through sulfur.[6]

Our interest in (polysulfido)ruthenium complexes stems mainly from the known special efficacy of ruthenium disulfide as a hydrodesulfurization catalyst[7] (e.g., RuS2 displays better oxygen

chemisorption and catalytic activity toward thiophene hydrodesulfurization than the conventional MoS2 catalyst).[7b] Additional

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Table I. Crystallographic Data for **1**

(PPh$_4$)[Ru(NO)(NH$_3$)(S$_4$)$_2$]	$T = 21$ °C
fw 744.0	$\lambda = 0.710\,73$ Å
space group $P2_1/n$	$\rho_{calcd} = 1.65$ g cm^{-3}
$a = 11.341$ (3) Å	$\mu = 11.28$ cm^{-1}
$b = 13.091$ (3) Å	transm coeff = 0.39 – 0.46
$c = 20.829$ (5) Å	$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\| = 0.046$
$\beta = 104.93$ (2)°	$R_w = (\sum w(\|F_o\| - \|F_c\|)^2/$
$V = 2987.8$ Å^3	$\sum w\|F_o\|^2)^{1/2} = 0.043$
$Z = 4$	$w^{-1} = \sigma^2(F) + 0.0001F^2$

incentive, however, comes from our long-range objective to prepare relatively less known transition-metal dinitrogen complexes with exclusive sulfur coligands, in view of the special relevance of the former in understanding the mode in which dinitrogen might bind or be reduced at the metal site (considered to be in the ligand field of sulfido groups)—a process widely believed to be taking place in nitrogenase.[8]

Through this communication we wish to report the first ruthenium complex with RuS$_4$ chelate rings that also has an ammine as well as a nitrosyl group in its coordination sphere. It is noteworthy that transition-metal nitrosyl complexes (which display their own catalytic activities in many useful processes[9]) have recently been used as models for the NO-"titrated" active sites in the promoted-hydrodesulfurization catalysts.[10]

Experimental Section

Synthesis. Though the product compound is air stable, all the manipulations were routinely carried out under a dry argon atmosphere. AR grade chemicals were purchased from commercial sources and used as received. Solvents were dried by standard methods. Hydrogen sulfide and ammonia gases were dried above CaCl$_2$ and KOH, respectively, before use.

Trichloronitrosylruthenium was generated in solution as reported elsewhere,[11a] and this solution was used directly in the reaction, assuming quantitative nitrosylation of hydrated ruthenium trichloride.

Tetraphenylphosphonium Polysulfide: (PPh$_4$)$_2$S$_n$. A moderate stream (6 L/h) of hydrogen sulfide gas was allowed to bubble, for ca. 1 min, through a vigorously stirred 100-mL ammoniacal acetonitrile solution (obtained by treating acetonitrile with a moderate stream of gaseous ammonia for 20 min) containing tetraphenylphosphonium bromide (2.52 g, 6 mmol) and sulfur (1.03 g, 32 mmol). A swift change in the color of the mixture from blue, through green, to brown was observed. The resulting mixture (A) was used directly in the following reaction.

(PPh$_4$)[Ru(NO)(NH$_3$)(S$_4$)$_2$] (1). To the freshly prepared mixture A was added 2 mL of an ethanolic solution of trichloronitrosylruthenium (ca. 0.25 mmol). After the contents of the reaction flask (which should be tightly closed) were stirred for 5 min, it was allowed to stand at room temperature. The crystalline solid that appeared over a period of 2 days was filtered out, washed carefully and successively with carbon disulfide (3 × 2 mL), methanol, and diethyl ether, and dried under a slow argon stream to yield 0.130 g of dark red-brown crystals (ca. 70%) of (PPh$_4$)[Ru(NO)(NH$_3$)(S$_4$)$_2$]. These were suitable for X-ray diffraction measurements. Anal. Calcd (found): C, 38.8 (38.3); H, 3.1 (3.4); N, 3.8 (3.8); S, 34.5 (35.2).

X-ray Structure Determination. The structure of **1** was determined from single-crystal X-ray diffraction data (Siemens R3m/V four-circle diffractometer). A summary of the crystal data and details concerning the intensity data collection and structure refinement are given in Table I. The unit cell parameters were obtained at 21 °C by the least-squares refinement of the angular settings of 16 high-angle reflections (19° < 2θ < 30°). An empirical absorption correction was applied. The data were corrected for Lorentz and polarization effects.

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Table II. Atomic Coordinates ($\times10^4$) for **1**

	x	y	z
Ru	4258 (1)	1609 (1)	914 (1)
N(1)	4050 (3)	1755 (3)	1697 (2)
O(1)	3846 (3)	1890 (3)	2208 (2)
N(2)	4403 (3)	1479 (3)	-90 (2)
S(1)	5115 (1)	3274 (1)	882 (1)
S(2)	6899 (1)	3109 (1)	1432 (1)
S(3)	7396 (1)	1825 (1)	1016 (1)
S(4)	6206 (1)	761 (1)	1232 (1)
S(5)	2323 (1)	2394 (1)	411 (1)
S(6)	1082 (1)	1262 (1)	453 (1)
S(7)	1820 (1)	76 (1)	58 (1)
S(8)	3455 (1)	-102 (1)	765 (1)
P	321 (1)	1288 (1)	3041 (1)
C(1)	2208 (2)	314 (1)	3944 (1)
C(2)	3233	294	4485
C(3)	3740	1207	4776
C(4)	3222	2139	4527
C(5)	2197	2159	3986
C(6)	1691	1246	3695
C(7)	-834 (2)	-223 (2)	2192 (1)
C(8)	-893	-976	1711
C(9)	159	-1260	1527
C(10)	1270	-791	1823
C(11)	1330	-38	2304
C(12)	278	246	2489
C(13)	762 (2)	2510 (2)	2050 (1)
C(14)	786	3436	1722
C(15)	316	4316	1942
C(16)	-178	4269	2489
C(17)	-202	3343	2817
C(18)	268	2463	2597
C(19)	-808 (2)	894 (2)	4042 (1)
C(20)	-1816	832	4307
C(21)	-2967	1122	3925
C(22)	-3109	1474	3277
C(23)	-2101	1536	3012
C(24)	-950	1246	3394

Table III. Bond Angles (deg) for the Anion in **1**

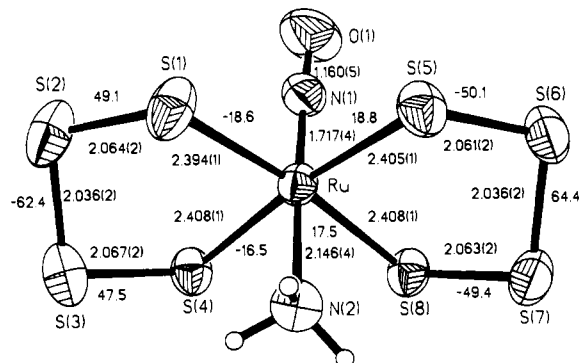|			
N(1)–Ru–N(2)	176.1 (1)	N(1)–Ru–S(1)	94.6 (1)
N(2)–Ru–S(1)	84.9 (1)	N(1)–Ru–S(4)	97.5 (1)
N(2)–Ru–S(4)	86.4 (1)	S(1)–Ru–S(4)	94.4 (1)
N(1)–Ru–S(5)	91.9 (1)	N(2)–Ru–S(5)	84.2 (1)
S(1)–Ru–S(5)	86.0 (1)	S(4)–Ru–S(5)	170.5 (1)
N(1)–Ru–S(8)	95.0 (1)	N(2)–Ru–S(8)	85.5 (1)
S(1)–Ru–S(8)	170.4 (1)	S(4)–Ru–S(8)	84.1 (1)
S(5)–Ru–S(8)	94.0 (1)	Ru–N(1)–O(1)	175.7 (3)
Ru–S(1)–S(2)	103.6 (1)	S(1)–S(2)–S(3)	100.9 (1)
S(2)–S(3)–S(4)	101.2 (1)	Ru–S(4)–S(3)	103.5 (1)
Ru–S(5)–S(6)	103.3 (1)	S(5)–S(6)–S(7)	100.0 (1)
S(6)–S(7)–S(8)	100.7 (1)	Ru–S(8)–S(7)	103.1 (1)
H–N–H	97 (4)–114 (3)		

Figure 1. Ellipsoid (50%) plot of the [Ru(NO)(NH$_3$)(S$_4$)$_2$]$^-$ anion in crystals of **1** with bond lengths (Å) and torsion angles (deg) within the RuS$_4$ rings.

The structure was solved by direct methods (SHELXTL-PLUS program package).[11b] After detection of the heavy atoms, the positional parameters of the remaining (except the PPh$_4$ hydrogen atoms) atoms were deduced from successive difference Fourier syntheses.

The phenyl rings of the cation were refined as rigid hexagons with hydrogen atoms (C–C = 1.395 Å, C–H = 0.96 Å, C–C–C = 120°, C–C–H = 120°). The hydrogen atoms of the NH_3 ligand were refined with a free temperature factor, and the N–H distance was fixed at 0.95 Å. The final least-squares refinements converged at the values given in Table I.

During the last cycles of refinement, no parameter shifted more than 0.1σ, where σ is the standard deviation of the parameter. The last difference Fourier synthesis showed no significant maxima.

The atomic scattering factors for all atoms were taken from standard sources.[11c] Anomalous dispersion corrections were applied to all atoms. Positional parameters are given in Table II. Selected bond lengths and angles are given in Figure 1 and Table III.

The experimentally measured X-ray powder diffraction pattern of **1** corresponds to that calculated from the single-crystal data, indicating that the bulk sample is substantially similar to the characterized single crystal.

Results and Discussion

The Structure. **1** has been characterized by X-ray structure analysis (Table I). An ellipsoid (50%) plot of the anion of **1** is shown in Figure 1 together with bond lengths and torsion angles; for bond angles see Table III. The ruthenium atom is located in an environment of a pseudooctahedral array of ligands consisting of two chelating tetrasulfido groups, which occupy all four equatorial positions around the metal atom, and one each of the nitrosyl and ammine group—taking axial positions. The Ru–N bond length (1.717 (4) Å) for the nitrosyl group, which is bonded through its nitrogen atom, is well in agreement with similar distances in those nitrosyl complexes of ruthenium(II) where nitrosyl groups are formally regarded as "NO^+".[12a] The Ru–N–O angle (175.7 (3)°) shows the presence of an approximately linear Ru–N–O moiety as expected for "NO^+". Ammonia, bonded to ruthenium with an Ru–N distance of 2.146 (4) Å, is trans to the nitrosyl group, giving rise to an essentially linear ON–Ru–NH_3 moiety (N–Ru–N = 176.1 (1)°). Both of the tetrasulfido groups are bonded to ruthenium through their terminal sulfur atoms, with all Ru–S distances being equal to 2.394 (1)–2.408 (1) Å. These closely resemble the Ru–S distances (2.375–2.415 Å) in the complexes [Ru(S$_2$CNEt$_2$)$_3$] and [Ru(NO)(S$_2$CNEt$_2$)$_3$][12b] and are notably longer than such distances in [(C$_5$Me$_4$Et)$_2$Ru$_2$S$_4$][12c] (2.195 (4) Å) and 1,5-[(MeCp)Ru(PPh$_3$)]$_2$S$_6$[12d] (2.267 (2)–2.376 (3) Å), where Ru–S multiple bondings have been proposed. The internal S–S distances in both of the five-membered metallacycles, which generate half-chair configurations (see Figure 1), are found to be approximately equal (2.036 (2)–2.067 (2) Å). This pattern is significantly different from that observed in the complex (PPh$_4$)[ReS(S$_4$)$_2$][12e] (1.997–2.146 Å). A half-chair M–S$_4$ ring conformation has also been found in [M(S$_4$)$_2$]$^{n-}$ ions (M = Ni, Pd, Zn, Hg) and in Cp$_2$Mo(S$_4$) and Cp$_2$W(S$_4$), whereas the ions [MoS(S$_4$)$_2$]$^{2-}$, [Mo$_2$S$_4$(S$_2$)(S$_4$)]$^{2-}$, [Mo$_2$S$_4$(S$_4$)$_2$]$^{2-}$, and [Cu$_4$(S$_4$)$_3$]$^{2-}$ possess M–S$_4$ rings with envelope configurations.[1a] A discussion of the possible reason is found in ref 12h. The N–O distance (1.160 (5) Å), which is comparable to the smaller value (1.170 Å) in [Ru(NO)(S$_2$CNEt$_2$)$_3$][12b] and slightly longer than the corresponding distance (1.142 Å) in [Ru(NO)Cl$_3$(PPh$_3$)$_2$],[12f] is consistent with the relatively lower observed value of ν(NO) (1808 cm^{-1}) in the IR spectrum of **1**.

Synthesis and Reactivity. Trichloronitrosylruthenium, conveniently formulated as [Ru(NO)Cl$_3$(H$_2$O)$_2$][12a,g] (**2**), which is formed when gaseous nitric oxide is bubbled through an ethanolic solution of hydrated ruthenium trichloride,[11a] is a useful starting material for synthesizing ruthenium nitrosyls. **2** reacts with excess ammonia to yield [Ru(NO)(NH$_3$)$_4$(OH)]Cl$_2$ (**3**).[12g] Since **1** also

Table IV. IR (CsI Pellet) and Raman (λ_e = 488 nm; Rotating Disk) Bands[a] of [Ru(NO)(NH$_3$)(S$_4$)$_2$]$^-$

IR freq, cm^{-1}	assgnt	Raman freq, cm^{-1}	assgnt
3320 w, b	ν(NH)	607 w	ν(Ru–NO)
3190 w, b	ν(NH)	527 w	ν(Ru–NO)
1808 vs	ν(NO)	483 w	ν(S–S)
1590 m	δ_{as}(NH$_3$)	448 s	ν(S–S)
1235 s	δ_s(NH$_3$)	351 m	ν_{as}(Ru–S)
760/750 w	ρ_r(NH$_3$)	299 s	ν_s(Ru–S)
570 m	ν(Ru–NO)		
458 m	ν(S–S)		
435 sh	ν(Ru–NH$_3$)		
334 w	ν(Ru–S)		

[a] Abbreviations used: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; b, broad.

contains an ammonia molecule coordinated to ruthenium, it is presumable that the formation of **1** proceeds via the formation of **3** or some other intermediate of a similar type. Other possibilities include the direct interaction of **2** with polysulfide ions, present in the reaction medium, resulting in the removal of chloro and aquo groups from the former with concomitant formation of two novel five-membered metallacycles by the incoming tetrasulfido moieties.

The ammonia molecule, present in the coordination sphere of **1**, is apparently derived from the ammoniacal acetonitrile medium used for preparing polysulfide ions. This assumption is corroborated by a recent report[13] in which the source of the ammine groups in [Cr(NH$_3$)$_2$(S$_5$)$_2$]$^-$ appears to be the ammoniacal methanolic solution of polysulfide ions.

Our attempts to precipitate the anion of **1** with other counterions (e.g. bis(triphenylphosphine)nitrogen(1+), tetramethylammonium, or tetraethylammonium) have, so far, resulted in failure. As yet, we have not succeeded in isolating other species with an n-membered metallacycle or metallacycles from the reaction mixture (where $n \neq 5$), despite the fact that there is a good possibility for the existence of S$_5^{2-}$ and other chelating species in the polysulfide solution. A recently reported[5a] eight-membered metallacyclic compound of ruthenium (containing the S$_7^{2-}$ group), obtained through a different synthetic route, further strengthens the possibility of the formation of such types of species in the present reaction medium also.

It has previously been suggested[14] that the polysulfido complexes which crystallize out may not necessarily be representative of the complexes present in the solution but are those favored by the lattice energy factor. It is, therefore, possible that the preferential crystallization of **1** from the solution might also have been guided by the lattice energy factor. Although the formation of binuclear species, with ruthenium atoms connected through a sulfido bridge or bridges, is not unlikely (such structures are well-known for iron,[1] and the complex [(C$_5$H$_4$Me)$_4$Ru$_4$S$_4$][15] also contains such bridging groups), it has so far illuded us.

1 is stable in air for months. Its acetonitrile solution seems to be unreactive toward molecular oxygen bubbling through it for several hours at room temperature whereas a small amount of gaseous nitric oxide decomposes **1** into an intractable product in a few hours. It is notable that complex **1** appears to be an interesting example of a metal nitrosyl in which the nitrosyl group, bonded to a coordinatively saturated metal center, is potentially liable to electrophilic attack. The latter types of reactions of the coordinated nitrosyl group are quite promising (e.g., the formation of an N–C bond from a metal nitrosyl has been demonstrated[9]).

Other Physicochemical Studies. The dark red-brown crystalline compound, whose microanalytical data satisfactorily correspond

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to its composition $C_{24}H_{23}N_2OPS_8Ru$, dissolves readily in organic solvents like dichloromethane, acetonitrile, and dimethylformamide, leading to stable solutions for hours at room temperature. The IR and Raman bands and their assignments are given in Table IV. All bands are in the expected region.

The diamagnetism of **1** is typical for an {RuNO}[6], system which gives rise to low-spin configurations. The positions of a broad band centered at 440 nm and another intense band at 350 nm in the electronic absorption spectrum (solid-state reflectance) are approximately similar to those observed in the case of *cis*-[Ru-$(NH_3)_4(NO)Cl]Cl_2$.[16]

The mass spectrum of the compound shows typically the fragmentation pattern of NH_3, with ion peaks corresponding to mass numbers 15, 16, and 17 besides all those expected from two S_4^{2-} groups.

It would be interesting to study the relation between the number of active sites on RuS_2 surfaces with different dispersions, determined by "titration" with NO, and HDS activity. This would answer the question of whether the Ru atoms or the S_2^{2-} groups are the active sites for the HDS process. In the case of promoted-HDS catalysts, an IR investigation of NO adsorption showed that the amount of NO adsorbed on cobalt edge atoms

("Co–Mo–S" atoms) is directly related to the promotion of catalytic activity.[10] The model for the nitrosylated HDS catalyst, $[Co(MoS_4)(NO)_2]^-$, exhibits $\nu(NO)$ bands with practically the same frequencies as those of the nitrosylated catalyst at the Co centers (for $[(NO)Mo(NCS)_4]^{2-}$ as corresponding model for the Mo centers, see refs 10 and 17) itself.[10]

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Crystal Structures and Characterization of a New Manganese(III) Arsenate, MnAsO₄·1.2H₂O, and Manganese(II) Pyroarsenate, Mn₂As₂O₇

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The synthesis and crystal structure of a new manganese(III) arsenate, MnAsO₄·1.2H₂O, are reported. This compound crystallizes in a monoclinic space group, C2/c (a = 7.030 (1) Å, b = 7.824 (1) Å, c = 7.469 (1) Å, β = 112.14 (1)°, Z = 4) and is isostructural with MnPO₄·H₂O. The structure has been refined from laboratory X-ray powder diffraction data by the Rietveld method (R_I = 3.3%, R_{WP} = 11.0%) and even the H position has been refined without constraints, showing that the water molecule is hydrogen-bonded to the arsenate groups. Whether the additional 0.2 water molecules are also present in the structure or in a second amorphous phase is unclear. A strong Jahn–Teller effect was found, in agreement with the diffuse-reflectance spectrum, and the TGA-DTA curves and the IR spectrum of the manganese(III) arsenate hydrate are discussed. The thermal decomposition product of MnAsO₄·1.2H₂O, manganese(II) pyroarsenate, Mn₂As₂O₇, crystallizes with a thortveitite-type structure (a = 6.7493 (8) Å, b = 8.7589 (8) Å, c = 4.7991 (5) Å, β = 102.83 (1)°, Z = 2, space group C2/m) and has been refined (R_I = 2.9%, R_{WP} = 6.7%) with a split-site model to take account of the disorder of the bridging oxygen due to bending of the pyroarsenate groups.

Introduction

Phosphates and arsenates of the first-row transition metals adopt a wide variety of stoichiometries and structure types and have been studied for their properties and applications. For instance, they may be used as catalysts, nonlinear optical materials, ionic exchangers, ionic conductors, and host compounds for intercalation reactions.

No synthetic or structural works have been reported on any manganese(III) arsenates, but some studies on manganese(III) phosphates have been published. The structure of MnPO₄·H₂O was determined from high-resolution synchrotron X-ray powder diffraction data,[2] and this compound has recently been studied by spectroscopic methods.[3] The crystal structures of the mixed-valence mineral bermanite, Mn₃(PO₄)₂(OH)₂·4H₂O,[4] manganese(III) metaphosphate, Mn(PO₃)₃,[5] manganese(III) hydrogen

pyrophosphate, MnHP₂O₇,[6] and two layered phosphates of manganese(III), KMn₂O(PO₄)(HPO₄)[7] and NH₄Mn₂O(PO₄)-(HPO₄)·H₂O,[8] are also known. Finally, H₂MnP₃O₁₀·2H₂O has recently been investigated by IR, diffuse-reflectance and X-ray absorption spectroscopies.[9]

As part of our study of phosphates and arsenates of manganese, we describe the synthesis, crystal structure, and a spectroscopic and thermal study of a new manganese(III) arsenate, MnAsO₄·1.2H₂O. The structure of the thermal decomposition product of MnAsO₄·1.2H₂O, manganese(II) pyroarsenate, Mn₂As₂O₇, has also been refined because a recent study using high-resolution powder neutron data gave a poor profile fit.[10]

Experimental Section

Manganese(III) arsenate hydrate was synthesized by slowly adding H₃AsO₄ (14 mL, 75% w/w in water) to a suspension of 7 g of manga-

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