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Inorganic Chemistry

Communications

Facile One-Step Synthesis of $Fe_4Q_4^{2+}$ (Q = S, Se) Cubane-like Centers[1]

Sir:

There have been a large number of syntheses reported for molecules containing the cubane-like core $Fe_4Q_4^{2+}$,[2-4] where Q = S or Se. Among such molecules, those with the general formula $Fe_4Q_4X_4^{2-}$ ($X = Cl^-, Br^-, I^-$) are of central importance because they provide starting materials for other $Fe_4Q_4^{2+}$ containing complexes with different terminal ligands, obtained by metathetical reactions (reaction 1).[3,5] Several synthetic routes have been

$$Fe_4Q_4X_4^{2-} + 4NaL \rightarrow Fe_4Q_4L_4^{2-} + 4NaX \quad (1)$$

reported[3,6-8] for the formation of sulfide containing clusters $Fe_4S_4X_4^{2-}$ (reactions 2–4). We report a new and particularly

$$Fe_4S_4(SR)_4^{2-} + 4PhC(O)X \rightarrow Fe_4S_4X_4^{2-} + 4PhC(O)SR \quad (2)$$

$$Fe_4(SR)_6Cl_4^{2-} + 4S \rightarrow Fe_4S_4Cl_4^{2-} + 3RSSR \quad (3)$$

$$4FeBr_3 + 5H_2S + 2Bu_4NBr \rightarrow (Bu_4N)_2Fe_4S_4Br_4 + (1/n)S_n + 10HBr \quad (4)$$

facile synthetic route to the complexes $Fe_4S_4Br_4^{2-}$ and $Fe_4Se_4Br_4^{2-}$. This synthesis is related to reaction 4 in that we employ solid anhydrous sodium chalcogenide salts, Na_2S and Na_2Se, in place of hydrogen chalcogenide gases, thus allowing for a precise control of the reaction stoichiometry. With the slow addition of Na_2S to a DMF solution of $FeBr_3$, the steps involved in the formation of $Fe_4S_4Br_4^{2-}$ can be followed easily by electronic absorption spectroscopy. From these data it has been possible to rationalize the formation of $Fe_4Q_4Br_4^{2-}$ (Q = S, Se).

The general method employed for the synthesis of $Fe_4Q_4Br_4^{2-}$ is illustrated for the sulfide-containing cluster. All steps were carried out at room temperature under a nitrogen atmosphere. In the preparation of $(Bu_4N)_2Fe_4S_4Br_4$ (**1**), the anhydrous reagents $FeBr_3$ (2.5 g, 8.45 mmol), Na_2S (0.82 g, 10.56 mmol), and Bu_4NBr (1.36 g, 4.23 mmol) were added with stirring to 30 mL of DMF. After 20 min the solution became dark brown. It was allowed to stir overnight. This solution was then filtered and the filtrate concentrated to dryness. The product was dissolved in 25 mL of CH_3CN, giving a dark brown solution, which was filtered and concentrated under vacuum to a volume of 15 mL. Ethyl ether (40 mL) was slowly added, and the product separated as lustrous black crystals. The product was recrystallized from CH_3CN and ethyl ether, affording a final yield of 1.7 g (71%). Anal. Calcd for $C_{32}H_{72}Br_4Fe_4N_2S_4$: C, 33.24; H, 6.28; S, 11.09. Found: C, 32.94; H, 6.06; S, 11.33. With $FeCl_3$ used as the source of iron, the Cl^--containing analogue of **1** was obtained by the same method in 50% yield. Use of Na_2Se as the chalcogenide source afforded the previously unreported product $(Et_4N)_2Fe_4Se_4Br_4$ (**2**) in 40% yield. Anal. Calcd for $C_{16}H_{40}Br_4Fe_4N_2Se_4$: C, 17.17; H, 3.60; Fe, 19.96; Se, 28.22. Found: C, 17.99; H, 3.72; Fe, 19.90; Se, 28.20.

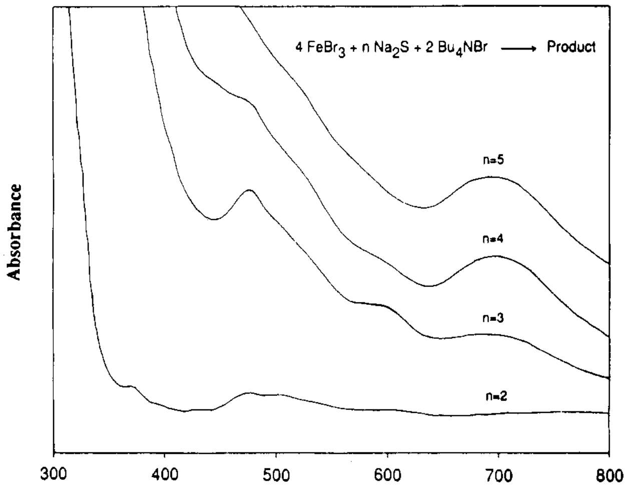

Figure 1. Electronic absorption spectra of the reaction system containing $FeBr_3$ and Na_2S in DMF, showing the formation of $Fe_2S_2Br_4^{2-}$ and $Fe_4S_4Br_4^{2-}$.

Two steps are observed in the formation of $Fe_4S_4Br_4^{2-}$ when Na_2S is added stepwise to a solution containing Bu_4NBr and $FeBr_3$. The first is a simple combination of sulfide ion with ferric bromide to form the dimer, $Fe_2S_2Br_4^{2-}$ ($\mathbf{3}^{2-}$) (reaction 5), as

$$2R_4NBr + 2FeBr_3 + 2Na_2S \rightarrow \underset{\mathbf{3}}{(R_4N)_2Fe_2S_2Br_4} + 4NaBr \quad (5)$$

evidenced by the unambiguous appearence of electronic absorption bands at 480, 598, and 700 (sh) nm.[3] The second is the one-electron reduction of dimer by sulfide ion and the resulting formation of tetramer **1** (reaction 6) with absorption bands at 500

$$2(R_4N)_2Fe_2S_2Br_4 + Na_2S \rightarrow \underset{\mathbf{1}}{(R_4N)_2Fe_4S_4Br_4} + 2R_4NBr + 2NaBr + (1/x)S_x \quad (6)$$

(sh), and 700 nm, (Figure 1). Redox-controlled formation of

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Table I. Selected Bond Distances and Angles for $Fe_4Se_4Br_4^{2-}$, $Fe_4Se_4(SPh)_4^{2-}$, and $Fe_4S_4Br_4^{2-}$

Selected Average Atomic Distances (Å)

$Fe_4Se_4Br_4^{2-}$ [a]			$Fe_4Se_4(SPh)_4^{2-}$ [b]			$Fe_4S_4Br_4^{2-}$ [c]		
atoms	set	av dist	atoms	set	av dist	atoms	set	av dist
Fe–Se	8	2.423[d]	Fe–Se	8	2.417	Fe–S	8	2.285
	4	2.370[e]		4	2.385		4	2.270
Fe–Fe	4	2.79	Fe–Fe	4	2.788	Fe–Fe	4	2.76
	2	2.77		2	2.773		2	2.755
Fe–Br	4	2.358	Fe–S	4	2.273	Fe–Br	4	2.342

Bond Angles (deg)

$Fe_4Se_4Br_4^{2-}$		$Fe_4Se_4(SPh)_4^{2-}$		$Fe_4S_4Br_4^{2-}$	
atoms	angles	atoms	angles	atoms	angles
Se–Fe–Se	108.7–103.9	Se–Fe–Se	108.6–104.6	S–Fe–S	103.9–102.5
Br–Fe–Se	118.4–108.3	S–Fe–Se	120.2–97.4	Br–Fe–S	117.2–112.2
Fe–Se–Fe	72.3–69.6	Fe–S–Fe	71.70–69.65	Fe–S–Fe	75.2–74.4

[a] This work. [b] Reference 2. [c] Reference 6. [d] Atom distances perpendicular to the S_4 axis of complex. [e] Atom distances parallel to the S_4 axis.

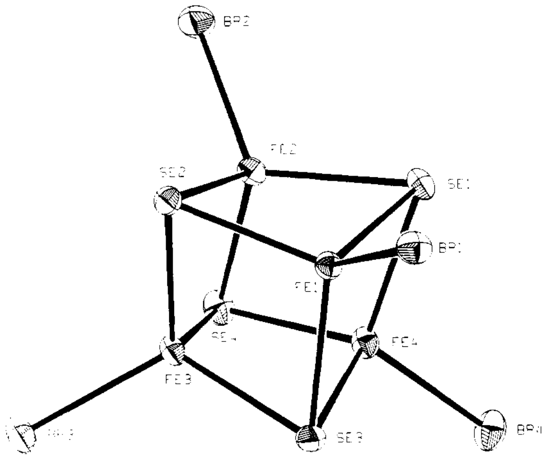

Figure 2. ORTEP drawing of $Fe_4Se_4Br_4^{2-}$ showing 30% thermal ellipsoids. Crystallographic data: space group $P2_1/c$ with $a = 13.899$ (5) Å, $b = 13.203$ (3) Å, $c = 18.703$ (7) Å, $\beta = 109.87$ (3)°, $V = 3228$ (4) Å^3, $Z = 4$, and $R = 0.076$ for 5977 unique reflections. Data were collected at −65 °C on an Enraf-Nonius CAD4F-11 diffractometer by using Mo Kα radiation.

tetramer has been reported by Wong et al. (1978).[3] Compound **3** disproportionates in DMF to form **1**. Absorption spectra show that the concentration of $Fe_2S_2Br_4^{2-}$ is maximal at a Na_2S:$FeBr_3$ ratio of 1:2. The $Fe_4S_4^{2+}$ tetramer becomes the predominant species at higher ratios. Reaction 6 therefore does not serve as a convenient route for the synthesis and isolation of product **3**, which could not be obtained in pure form. The analogous stepwise reaction is not observed in the formation of product **2**. This is presumably due to disproportionation of the iron–selenide dimer. Compound **2** was identified by the ^1H NMR spectrum of its derivative $(Bu_4N)_2Fe_4Se_4(SPh)_4$ (**4**) in CD_3CN (m-H, 8.36 ppm; p-H, 4.87 ppm; o-H, 5.51 ppm)[9] obtained via the metathetical reaction between **3** and 4 equiv of NaSPh in CH_3CN.

In the absence of added tetralkylammonium counterion, $Fe(DMF)_6^{2+}$ formed as a counterion. The product $Fe(DMF)_6Fe_4S_4Br_4$ (**5**) was isolated as a crystalline solid by reaction 7 followed by a standard workup as detailed above. In the ^1H NMR spectra, the counterion of **5** in CD_3CN gives a broad methyl group signal at 3.4 ppm. The formyl proton signal was absent, perhaps due to extensive broadening. Infrared spectra of **5** prepared in a KBr pellet revealed DMF carbonyl bands at 1653, 1648, 1637, and 1669 cm^{-1}, congruent with those of the perchlorate salt of $Fe(DMF)_6^{2+}$, which has DMF carbonyl bands at 1655, 1650, and 1640 cm^{-1}.[10]

$$5FeBr_3 + {}^{11}/{}_2Na_2S \xrightarrow[DMF]{} [Fe(DMF)_6]Fe_4S_4Br_4 + 11NaBr + (3/2x)S_x \quad (7)$$

The absorption spectrum of **1** exhibits bands at 700 (1900), 525 (2300), and 282 (20 000) nm (cm^{-1} M^{-1}).[3] By virtue of position and intensity they correspond to bands in the spectrum of **2** at 746 (1970), 560 (2820), and 295 (23 650) nm (cm^{-1} M^{-1}). There are additional bands at 250 (28 450) and 218 (35 200) nm (cm^{-1} M^{-1}), for which no corresponding bands have been reported in the literature. All of the absorption bands for the selenido complex are red shifted relative to the corresponding ones of the sulfido complex. By use of the Evans method,[13] a magnetic susceptibility of 2.19 μ_B (302 K) is found for compound **2**. This is in the range of 2.1–2.5 μ_B (299 K) found for related $Fe_4Q_4^{2+}$ complexes.[2,3] Structurally, $(Et_4N)_2Fe_4Se_4Br_4$ (Figure 2) is unexceptional as may be judged from the table of selected bond angles and distances (Table I). The structure contains an S_4 axis roughly parallel to the four short Fe–Se bonds (Table I), common to cubane-like iron–chalcogenide ions in the 2− oxidation state.[2,6]

Relative ease of formation may be an important factor in the occurrence of $Fe_2S_2^{2+}$ and $Fe_4S_4^{2+}$ centers as prosthetic groups in proteins. Recent studies provide evidence that iron–sulfur protein renaturation involves the formation and insertion of intact iron–sulfur cores.[14-16] The observation of stepwise direct assembly of synthetic iron chalcogenide complexes from Fe^{3+} and S^{2-} ions in solution as reported in this work suggests a similar route for the formation of iron–sulfur cores in the cellular environment.

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Supplementary Material Available: General structure report for compound **2**, including details of the structure determination, listings of experimental details, positional and thermal parameters, inter- and intramolecular distances and bond angles involving nonhydrogen atoms, and intermolecular distances involving hydrogen atoms, and ORTEP and PLUTO drawings of the structure (27 pages); a listing of final and observed

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structure factors (21 pages). Ordering information is given on any current masthead page.

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Anaerobic Oxidation of Cobalt(II) Protoporphyrin IX Dimethyl Ester[1] in Basic Methanolic Solution

Sir:

In alcoholic solutions, in the presence of molecular oxygen, and in the presence of various amine ligands (L), the oxidation of cobalt(II) protoporphyrin IX dimethyl ester,[1] [$Co^{II}P$], proceeds readily[2,3] by way of the reaction intermediate [$Co^{II}P(L)(O_2)$], the involvement of which has been widely recognized.[4–7] Even in absence of amine ligands [$Co^{II}P$] in methanol undergoes oxidation yielding mainly [$Co^{III}P(CH_3O)(CH_3OH)$] at a rate 10^2–10^3 times smaller than that with amine ligands.[8,9] In this case coordinated methanol acts as a weak electron donor, promoting electron transfer from cobalt to molecular oxygen. We now report that the best electron donors for promoting oxidation of [$Co^{II}P$] are coordinated alkoxides (methoxide < isopropoxide < *sec*-butoxide) dissolved in aliphatic alcohols. We noticed earlier[8,9] that the methoxide group in the [$Co^{III}P(MeO)$] intermediate strongly increases the electron density in the *trans* axial position, which favored the entry of the least basic amine ligand (not the most basic, as usually observed). But the most unexpected consequence of the excellent electron-donor ability of the methoxide ligand is the fact that a methanolic solution of [$Co^{II}P$] in presence of CH_3O^- yields [$Co^{III}P(CH_3O)_2$]$^-$, even in the absence of oxygen. The spectra of methanolic solutions of [$Co^{II}P$] and of [$Co^{III}P(CH_3OH)(CH_3O)$] are known.[9] The latter complex can be prepared either by the reaction of [$Co^{II}P$] with methanol and molecular oxygen in methanolic solution, or by solvolysis of [$Co^{III}P(Cl)$] in methanol.[9] If methoxide is added to the methanolic solution of [$Co^{III}P(CH_3OH)(CH_3O)$], in air, the dimethoxide complex, [$Co^{III}P(CH_3O)_2$], is formed. (The latter complex tends to slowly μ-dimerize. The rate of dimerization depends on the methoxide concentration. The dimer might be μ-methoxo-bridged cobalt(III)—analogous with μ-hydroxo-bridged iron(III) porphyrins.[10]) Curve 2 in Figure 1 shows the spectrum of methanolic solutions of [$Co^{III}P(CH_3O)_2$]$^-$ (Soret, 423 nm; α, 573 nm; β, 537 nm); curve 1 is the spectrum of [$Co^{III}P(CH_3OH)(CH_3O)$]. If methoxide is added to a methanolic solution of [$Co^{II}P$], several reactions will take place, which was inferred from the rates of [$Co^{II}P$] disappearance. At zero methoxide concentration k_{obsd} for the formation of [$Co^{III}P(CH_3OH)(CH_3O)$] from [$CO^{II}P$] is 0.8×10^{-4} s^{-1} at 25 °C. The first addition of sodium methoxide reduces the reaction rate, and the minimum rate is achieved at 5×10^{-4} mol dm^{-3} CH_3O^-. At this methoxide concentration the methanolic solutions of [$Co^{II}P$] show no spectral changes during several days.

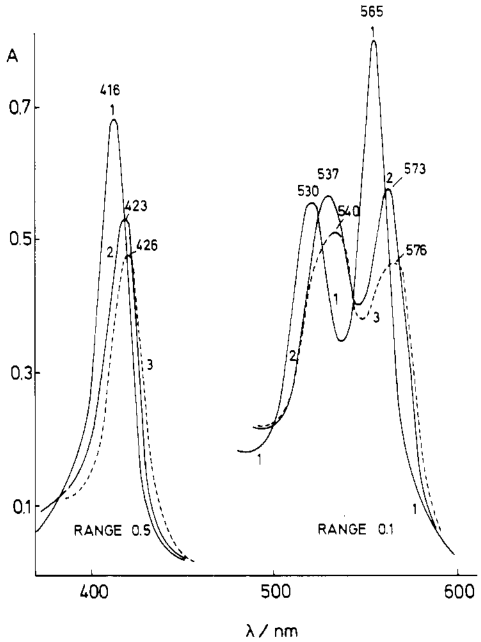

Figure 1. Absorption spectra of 5×10^{-6} mol dm^{-3} [$Co^{III}P(CH_3O)(CH_3OH)$] (1) and of [$Co^{III}P(CH_3O)_2$]$^-$ (2) in methanol (+3% v/v chloroform). Spectrum 2 changes to the dashed spectrum (3), supposedly corresponding to the cobalt(III) μ-methoxo-bridged dimer (N.B.: the β peak is larger than the α peak).

The rate decrease is expected since protons are needed for elimination of coordinated O_2 as $HO_2^{\bullet}$. The "directing" ligand is still coordinated methanol. Further increase of CH_3O^- concentration causes replacement of coordinated methanol with methoxide, and the rate goes up, in spite of the decrease of proton concentration, because coordinated alkoxides are among the best electron donors known. In strongly basic solutions (concentration of CH_3O^- > 1.0 mol dm^{-3}) the rates of aerobic and anaerobic oxidation tend to become equal, suggesting that at this methoxide concentration the same mechanism operates in both cases. The saturation rates are obtained when all coordinated methanol is replaced by methoxide. The spectrum of the reaction product is that of [$Co^{III}P(CH_3O)_2$]$^-$.

We are much surprised to find that [$Co^{II}P$] (5×10^{-6} mol dm^{-3}) and CH_3O^- (0.5 mol dm^{-3}), under oxygen-free argon, produced exactly the same spectrum as that of [$Co^{III}P(CH_3O)_2$]$^-$. Figure 2 shows the spectral changes of a solution of [$Co^{II}P$] (5×10^{-6} mol dm^{-3}) and methoxide (0.5 mol dm^{-3}) in methanol (3–5% v/v of benzene) in oxygen-free argon. The Soret maximum moves, in about 5 h, from 402 to 423 nm; the α and β peaks move simultaneously from 557 and 528 to 573 and 537 nm, respectively. The peaks at 423, 573, and 537 nm are absorption maxima of [$Co^{III}P(CH_3O)_2$]$^-$; see Figure 1. No doubt, in the absence of oxygen, it is the methoxide that is responsible for the electron transfer from Co(II), because we found the same spectral changes with isopropoxide and *sec*-butoxide. The electron-donating strength of the coordinated (directing) ligand must be important since several other investigated ligands (pyridine, imidazole, piperidine, azide, thiocyanate) did not cause any spectral changes of methanolic solutions of [$Co^{II}P$] under oxygen-free argon. For kinetic measurements, in the absence of oxygen, very pure argon (99.999%) was further purified by passing it through a cylindrical glass column, inside diameter 7 cm and height 90 cm, filled with chromium(II) salts dispersed on silica. An Oxi 9 apparatus with an E 090 WTW O_2-membrane electrode (provided by Labor Center, Nürnberg) could not detect any O_2 in a water sample saturated with argon purified as described; on the basis of instrument sensitivity it was inferred that the O_2 concentration was <10 μg dm^{-3}. The apparatus for the work in oxygen-free argon was previously described.[9] Because the concentration of O_2 in the solution was $\leq 3 \times 10^{-7}$ and the concentration of the complexes were 5×10^{-6} mol dm^{-3}, there was not enough oxygen for Co(II)

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