valence band as would occur for a semimetal.

These new layered chalcogenides have Ta or Nb in a high formal oxidation state; this should afford a set of empty d orbitals capable of accepting electrons. As with other layered transition-metal chalcogenides, insertion of electron donors into the van der Waals' gap may be possible. Moreover the presence of electron-rich Pd atoms within the layers may allow for insertion of electron acceptors under appropriate experimental conditions. To date we have found an extensive chemistry associated with the layers themselves; these results will be summarized in a forthcoming report.[18]

Acknowledgment. This research was supported by the National Science Foundation, Solid State Chemistry, Grant No. DMR83-15554. Some of the powder measurements were made in the X-ray Facility of Northwestern University's Material Research Center, supported in part under the NSF-MRL program (Grant No. DMR82-16972). S.M. thanks Academia Sinica and the U.S.-China program of the National Science Foundation (Grant No. INT81-17267) for support.

Registry No. Ta_2PdS_6, 97314-96-0; Ta_2PdSe_6, 97314-97-1; Nb_2PdS_6, 97314-94-8; Nb_2PdSe_6, 97314-95-9.

Supplementary Material Available: Tables of anisotropic thermal parameters and structure amplitudes (×10) for Ta_2PdSe_6 (Tables IV and V) and Ta_2PdS_6 (Tables VI and VII) (14 pages). Ordering information is given on any current masthead page.

---

(18) Keszler, D. A.; Ibers, J. A. *J. Am. Chem. Soc.*, in press.

Contribution from the Lehrstuhl für Anorganische Chemie I, Ruhr-Universität, D-4630 Bochum, FRG,
and Anorganisch-Chemisches Institut der Universität, D-6900 Heidelberg, FRG

Preparation and Crystal Structure of Bis(1,4,7-trithiacyclononane)iron(II) Bis(hexafluorophosphate) Containing an Octahedral, Low-Spin $Fe^{II}S_6$ Core. Electrochemistry of $[M([9]aneS_3)_2]^{2+}$ Complexes (M = Fe, Co, Ni)

KARL WIEGHARDT,*[†] HEINZ-JOSEF KÜPPERS,[†] and JOHANNES WEISS[‡]

Received December 6, 1984

The preparation of red $[Fe^{II}([9]aneS_3)_2](PF_6)_2$ ($[9]aneS_3$ = 1,4,7-trithiacyclononane, $C_6H_{12}S_3$) containing an octahedral, low-spin $Fe^{II}S_6$ core is reported. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 7.636$ (1) Å, $b = 10.314$ (2) Å, $c = 15.445$ (4) Å, $\beta = 92.96$ (2)°, $V = 1215$ (1) Å^3, and $d_{calcd} = 1.931$ g/cm^3 for $Z = 2$ and molecular weight 706.5. Least-squares refinement of the structure based on 2977 observations led to final discrepancy indices of $R = 0.045$ and $R_w = 0.049$. The structure consists of discrete cations $[Fe([9]aneS_3)_2]^{2+}$, with a nearly regular octahedral FeS_6 core, and PF_6^- anions. The electronic solution spectrum is consistent with a d^6 low-spin electronic configuration. The ligand field strength of $[9]aneS_3$ is comparable with that of its nitrogen analogues 1,4,7-triazacyclononane and 2,2′-bipyridine. Cyclic voltammograms of $[Fe([9]aneS_3)_2]^{2+}$ and $[Ni([9]aneS_3)_2]^{2+}$ in acetonitrile exhibit a reversible and a quasi-reversible one-electron-transfer reaction, respectively, at +0.98 and +0.97 V vs. Fc^+/Fc, which is similar to the irreversible oxidation of the uncoordinated ligand (E_{ox} = +0.99 V vs. Fc^+/Fc). Oxidation of a coordinated ligand is suggested rather than oxidation of the metal centers. In contrast, the cyclic voltammogram of $[Co([9]aneS_3)_2]^{2+}$ exhibits two reversible one-electron-transfer processes at formal redox potentials of −0.013 and −0.86 V vs. Fc^+/Fc, which correspond to the couples $[Co([9]aneS_3)_2]^{3+/2+}$ and $[Co([9]aneS_3)_2]^{2+/+}$, respectively. Magnetic susceptibility measurements indicate a low-spin d^7 configuration ($t_{2g}^6e_g^1$) for $[Co([9]aneS_3)_2]^{2+}$ and a d^6 low-spin arrangement ($t_{2g}^6e_g^0$) for $[Fe([9]aneS_3)_2]^{2+}$, whereas $[Ni([9]aneS_3)_2]^{2+}$ is paramagnetic with two unpaired electrons per Ni(II).

Introduction

It has been recognized recently that the cyclic triamine 1,4,7-triazacyclononane exerts a surprisingly high ligand field (LF) strength, the origin of which is controversial.[1-3] The preparation and structural characterization of the octahedral low-spin iron(II) and iron(III) bis complexes[4] $[Fe([9]aneN_3)_2]^{2+}$ and $[Fe([9]aneN_3)_2]^{3+}$ have supported the view that this is a real electronic effect.

In contrast, the coordination chemistry of the trithia analogue 1,4,7-trithiacyclononane ($[9]aneS_3$) has been explored to a much lesser degree due to the prohibitively low yields of the original syntheses.[5,6] Sellmann et al. have recently published an elegant template synthesis for this interesting ligand in good yields.[7]

It is of interest to compare the LF strength of this facially coordinating ligand with that of its nitrogen-donor analogue. Simple thioether ligands are usually considered to be weak ligands.[8] We here report the synthesis, electrochemistry, and crystal structure of the low-spin complex $[Fe([9]aneS_3)_2]^{2+}$. In addition, we have further characterized the complexes $[Ni([9]aneS_3)_2]^{2+}$ and $[Co([9]aneS_3)_2]^{2+}$[6] by their electronic spectra and magnetic moment measurements.

Experimental Section

Materials. The ligand 1,4,7-trithiacyclononane was synthesized by Sellmann's method.[7] $[Ni([9]aneS_3)_2](BF_4)_2$ and $[Co([9]aneS_3)_2](BF_4)_2$ were prepared by the literature procedure.[6]

Preparation of $[Fe([9]aneS_3)_2](ClO_4)_2$. (a) To a solution of 1,4,7-trithiacyclononane ($[9]aneS_3$) (0.18 g) in 20 mL of methanol was added with stirring a solution of $Fe(ClO_4)_3\cdot 6H_2O$ (0.26 g) in 10 mL of methanol. This solution was heated for 4 h to 50 °C, during which time its color changed to purple. Purple crystals precipitated upon cooling to 0 °C, which were filtered off, washed with ethanol and ether, and air-dried. Recrystallization from a minimum amount of water was achieved by addition of $NaClO_4$, and the hexafluorophosphate salt was precipitated by addition of $NaPF_6$.

(b) An identical product was obtained from argon-scrubbed methanolic solutions of $FeCl_2\cdot 4H_2O$ with the same reaction conditions as described above. Anal. Calcd for $C_{12}H_{24}S_6FeCl_2O_8$: C, 23.13; H, 4.14; S, 30.28; Fe, 9.35. Found: C, 23.3; H, 3.9; S, 30.8; Fe, 9.1. ^1H NMR (60 MHz, Me_2SO-d_6): $\delta(CH_2)$ = 3.01 (s).

[†] Ruhr-Universität.

[‡] Universität Heidelberg.

(1) Yang, R.; Zompa, L. J. *Inorg. Chem.* **1976**, *15*, 1499.

(2) Alper, J. S.; Zompa, L. J. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1693.

(3) Hart, S. M.; Boeyens, J. C. A.; Hancock, R. D. *Inorg. Chem.* **1983**, *22*, 982.

(4) (a) Wieghardt, K.; Schmidt, W.; Herrmann, W.; Küppers, H.-J. *Inorg. Chem.* **1983**, *22*, 2953. (b) Boeyens, J. C. A.; Forbes, A.; Hancock, R. D.; Wieghardt, K. *Inorg. Chem.*, in press.

(5) (a) Gerber, D.; Chongsawangvirod, P.; Leung, A. K.; Ochrymowycz, L. A. *J. Org. Chem.* **1977**, *42*, 2645. (b) Glass, R. S.; Wilson, G. S.; Setzer, W. N. *J. Am. Chem. Soc.* **1980**, *102*, 5068.

(6) Setzer, W. N.; Ogle, C. A.; Wilson, G. S.; Glass, R. S. *Inorg. Chem.* **1983**, *22*, 266.

(7) Sellmann, D.; Zapf, L. *Angew. Chem.* **1984**, *96*, 799. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 807.

(8) Murray, S. G.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 365.

0020-1669/85/1324-3067$01.50/0 © 1985 American Chemical Society

Table I. Crystallographic Data and Data Collection Parameters at 22 °C

formula	$C_{12}H_{24}S_6FeP_2F_{12}$
fw	706.5
space group	$P2_1/c$
a, Å	7.636 (1)
b, Å	10.314 (2)
c, Å	15.445 (4)
β, deg	92.96 (2)
V, Å^3	1215 (1)
Z	2
d_{calcd}, g/cm^3	1.931
cryst size, mm	0.5 × 0.5 × 0.5
μ(Mo Kα), cm^{-1}	31.3
diffractometer	AED II-Siemens
radiation	Mo Kα (graphite monochromator)
scan method	ϕ–2ϕ, $3 < 2\phi < 60°$
no. of reflcns	3532
no. of unique data ($I > 2.5\sigma(I)$)	2977
no. of variables refined	151
std reflcns	2 every 150 reflcns, no decay obsd
octants	$\pm h,k,l$
max shift/esd, final cycle	0.9
R	0.045
R_w	0.049

Table II. Atomic Coordinates (×10^4) of $[Fe([9]aneS_3)_2](PF_6)_2$

atom	*x/a*	*y/b*	*z/c*
Fe	0	0	0
P	4033 (1)	7 (1)	3234 (1)
S(1)	1477 (1)	1449 (1)	847 (1)
S(2)	7688 (1)	194 (1)	827 (1)
S(3)	1033 (1)	−1647 (1)	844 (1)
F(1)	3462 (5)	−307 (3)	418 (2)
F(2)	2080 (4)	−265 (4)	2885 (3)
F(3)	4490 (5)	−1453 (3)	3109 (2)
F(4)	3519 (4)	1494 (2)	3373 (2)
F(5)	4572 (4)	331 (3)	2286 (2)
F(6)	5979 (4)	333 (3)	3575 (2)
C(1)	−3587 (4)	1533 (3)	372 (3)
C(2)	1524 (4)	2892 (3)	173 (2)
C(3)	211 (5)	−3144 (3)	338 (3)
C(4)	3345 (4)	−1680 (3)	591 (3)
C(5)	−1380 (5)	893 (4)	1826 (2)
C(6)	−37 (5)	1949 (3)	1671 (2)

The perchlorate salts $[Ni([9]aneS_3)_2](ClO_4)_2$ and $[Co([9]aneS_3)_2](ClO_4)_2$ were prepared analogously with $Ni(ClO_4)_2 \cdot 6H_2O$ and $Co(ClO_4)_2 \cdot 6H_2O$ as starting materials.

Preparation of $[Fe([9]aneS_3)Cl_3]$. To a solution of $[9]aneS_3$ (0.18 g) in 20 mL of methanol was added dropwise with stirring a solution of $FeCl_3 \cdot 6H_2O$ (0.27 g) in 10 mL of methanol. Red crystals precipitated immediately, which were filtered off, washed with methanol and ether, and air-dried. Anal. Calcd for $C_6H_{12}S_3FeCl_3$: C, 21.04; H, 3.53; S, 28.08. Found: C, 20.9; H, 3.6; S, 27.9.

X-ray Structural Determination of $[Fe([9]aneS_3)_2](PF_6)_2$. A red, nearly cubic crystal of $[Fe([9]aneS_3)_2](PF_6)_2$ was attached to the end of a glass fiber and mounted on an AED II Siemens four-circle diffractometer. Preliminary examinations showed that the crystal belonged to the monoclinic system, space group $P2_1/c$. The unit cell dimensions (22 °C) were obtained by a least-squares fit of 40 reflections. The data are summarized in Table I. Intensity data were measured at 22 °C by ϑ–2ϑ scans and were corrected for Lorentz and polarization effects. An empirical absorption correction was carried out.[9a] The structure was solved via three-dimensional Patterson and Fourier syntheses. Idealized positions of the methylene H atoms were calculated on the basis of d(C–H) of 0.96 Å for sp^3-hybridized C atoms and included in the refinement cycles with isotropic thermal parameters. The function minimized during least-squares refinements was $\sum w(|F_o| - |F_c|)^2$ with final convergence to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.045$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.049$ ($w = 1/\sigma^2(F)$). Scattering factors for all atoms were taken from ref 9b. The real and imaginary parts of anomalous dispersion for all atoms were included.[9b] A final difference Fourier synthesis was essentially featureless. The final atomic paramters are given in Table II and bond distances and angles in Table III. Lists of observed and calculated structure factors, anisotropic thermal parameters, and coordinates of H atoms are available as supplementary material.

Table III. Selected Bond Distances (Å) and Angles (deg) of the Cation $[Fe([9]aneS_3)_2]^{2+}$

Fe–S(1)	2.251 (1)	S(1)–C(2)	1.817 (3)
Fe–S(2)	2.241 (1)	S(1)–C(6)	1.836 (3)
Fe–S(3)	2.259 (1)	S(2)–C(1)	1.811 (4)
C(1)–C(4A)	1.517 (6)	S(2)–C(5)	1.814 (4)
C(2)–C(3A)	1.529 (5)	S(3)–C(3)	1.827 (3)
C(5)–C(6)	1.523 (5)	S(3)–C(4)	1.828 (4)
S(1)–Fe–S(1A)	178.3 (9)	S(1)–Fe–S(3A)	89.2 (1)
S(1)–Fe–S(2)	89.7 (1)	S(2)–Fe–S(2A)	180
S(1)–Fe–S(2A)	90.3 (1)	S(3)–Fe–S(3A)	180
S(1)–Fe–S(3)	90.8 (1)	S(2)–Fe–S(3A)	90

Table IV. Electronic Spectra[d] and Magnetic Moments of Complexes

complex	λ, nm (ε, L mol^{-1} cm^{-1})	μ_{eff}(298 K), μ_B	ref
$Ni([9]aneS_3)_2^{2+}$	784 (27), 527 (26), 325 (14 000)	3.05	this work
$Ni([9]aneN_3)_2^{2+}$	870 (sh), 800 (7), 505 (5), 308 (12)	2.8	1
$Co([9]aneS_3)_2^{2+}$	730 (11), 560 (sh), 480 (92), 338 (6600), 264 (6500)[a]	1.82	this work
$Co([9]aneN_3)_2^{2+}$	850 (2.4), 630 (1.4), 545 (sh), 462 (5.9), 318 (sh)	4.8	4
$Fe([9]aneS_3)_2^{2+}$	523 (53), 395 (52)	*b*	this work
$Fe([9]aneN_3)_2^{2+}$	601 (6), 387 (17), 288 (560)	diamag	4
$Fe([9]aneS_3)Cl_3$	492[c]	5.92	this work

[a] Measured in acetonitrile. [b] Diamagnetic in solution: $[Fe([9]aneS_3)_2](ClO_4)_2$ μ_{eff} = 0.65 (100 K) and 1.23 μ_B (298 K). [c] Reflectance spectrum. [d] Measured in H_2O.

Electrochemistry. The apparatus used for cyclic voltammetric measurements has been described previously.[4] Cyclic voltammograms were measured in purified acetonitrile.[10] The supporting electrolyte was in all cases a 0.1 M solution of tetra-*n*-butylammonium hexafluorophosphate in CH_3CN. At the beginning of each experiment a cyclic voltammogram of the solution containing only the supporting electrolyte was measured under an argon atmosphere. To this solution were added and dissolved with stirring solid samples to yield 10^{-3} M concentrations of the respective materials. Cyclic voltammograms were recorded at scan rates from 10 to 500 mV s^{-1}. Then an equimolar amount of ferrocene was added as internal standard. Formal redox potentials are given vs. the reference system ferrocenium/ferrocene (Fc^+/Fc) in volts.

Instrumentation. The magnetic susceptibilities of powdered samples were measured by using the Faraday method between 98 and 298 K (Sartorius microbalance, Bruker B-E 10C8 research magnet, and Bruker B-VT 1000 automatic temperature control). Diamagnetic corrections were applied with use of published tables.

Electronic spectra of complexes were recorded on a Perkin-Elmer Lambda 9 spectrophotometer.

Results and Discussion

Preparation and Magnetic Properties. The bis(1,4,7-trithiacyclononane) complexes of Fe^{II}, Co^{II}, and Ni^{II} were prepared as the perchlorate salts from methanolic solutions of the ligand and the respective $M(ClO_4)_2 \cdot 6H_2O$ salt at 50 °C in the molar ratio of 2:1. When $Fe(ClO_4)_3 \cdot 6H_2O$ was used as starting material, reduction of the iron(III) center by the ligand and formation of $[Fe([9]aneS_3)_2]^{2+}$ was observed at 50 °C within 4 h. When $FeCl_3 \cdot 6H_2O$ and $[9]aneS_3$ (1:1) were reacted in methanol at room temperature, the red neutral complex $Fe([9]aneS_3)Cl_3$ precipitated.

The magnetic susceptibilities of powdered samples of perchlorate salts were measured in the temperature range 98–293 K with use

---

(9) (a) Computations were performed on a NOVA 3 (General Data) computer using the SHELXTL crystallographic calculation program (Sheldrick, G. M. "SHELXTL"; Universität Göttingen; Revision 3.0 (1981)). (b) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(10) Walter, M.; Ramaley, L. *Anal. Chem.* **1973**, *45*, 165.

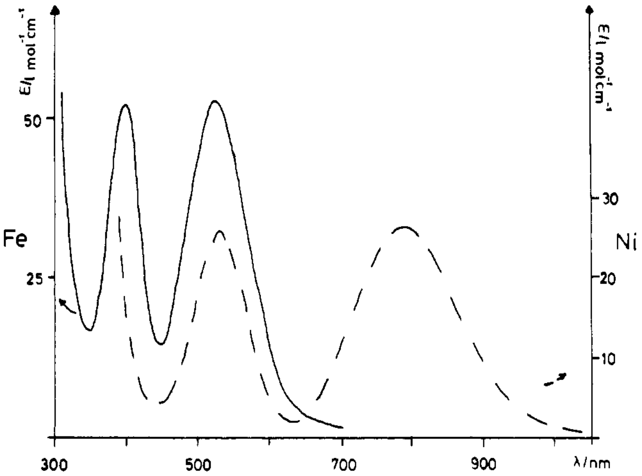

Figure 1. Electronic spectrum of $[Fe([9]aneS_3)_2]^{2+}$ (—) and of $[Ni([9]aneS_3)_2]^{2+}$ (---) in H_2O.

of the Faraday method. Effective magnetic moments are given in Table IV. $Fe([9]aneS_3)Cl_3$ exhibits normal Curie behavior; it is paramagnetic and has a temperature-independent magnetic moment of 5.92 μ_B, which is typical for a high-spin d^5 electronic configuration.

$[Ni([9]aneS_3)_2](ClO_4)_2$ has a magnetic moment of 3.05 μ_B in the temperature range employed indicative of a d^8 electronic configuration in an octahedral ligand field.

The magnetic moment of $[Co([9]aneS_3)_2](ClO_4)_2$ was found to be 1.82 μ_B between 100 and 298 K. This indicates a low-spin d^7 electronic configuration of Co(II) ($t_{2g}^6e_g^1$). In constrast, the nitrogen analogue $[Co([9]aneN_3)_2]^{2+}$ is high-spin ($t_{2g}^5e_g^2$).[4]

Finally, the $[Fe([9]aneS_3)_2]^{2+}$ species was found to be diamagnetic in Me_2SO-d_6 solution. In the 60-MHz ^1H NMR spectrum a singlet due to methylene protons is observed at δ 3.01. From magnetic susceptibility data of solid samples of the PF_6^- and ClO_4^- salts small temperature-dependent effective magnetic moments between 0.5 and 2.6 μ_B were deduced. These values were dependent on the preparation of samples and may be indicative of small impurities of Fe(III) or, alternatively, a singlet–triplet spin-state equilibrium as has been reported for $[Fe(Me_2Dtc)_2TFD]$ (Me_2Dtc = *N*,*N*-dimethyldithiocarbamate and TFD = bis(perfluoromethyl)-1,2-dithietene).[15]

The octahedral $[Fe([9]aneN_3)_2]Br_2 \cdot 3H_2O$ is diamagnetic in the solid state,[4] but removal of water of crystallization under vacuum yields a paramagnetic sample, and temperature-dependent magnetic susceptibility measurements suggest a spin-crossover behavior.[11]

Electronic Spectra. Figure 1 shows the electronic spectrum of $[Fe([9]aneS_3)_2]^{2+}$ exhibiting two d–d absorption maxima typical of low-spin Fe(II) in an octahedral ligand field,[12,13] which are not obscured by intense charge-transfer bands of the metal-to-ligand type as is often the case in Fe(II) complexes with aromatic or unsaturated nitrogen-donor ligands. From the energy difference of these two maxima, which is approximately $16B$, and assuming $C = 4B$, Dq is calculated to be 2067 cm^{-1} and B = 387 cm^{-1}:[13]

$$A_{1g} \rightarrow T_{1g} = 10Dq - C \qquad A_{1g} \rightarrow T_{2g} = 10Dq + 16B - C$$

For the analogous $[Fe([9]aneN_3)_2]^{2+}$[4] Dq is determined to be 1894 cm^{-1} and B = 575 cm^{-1}. These Dq values are in good agreement with those reported by Busch et al.[12] for low-spin Fe(II) complexes containing saturated tetraaza macrocycles.

The electronic spectrum of $[Ni([9]aneS_3)_2]^{2+}$ (Table IV, Figure 1) measured by us in H_2O is not in agreement with that reported previously[6] (measured in nitromethane), where the low-energy transition at 784 nm ($^3A_{2g} \rightarrow {}^3T_{2g}$) had not been detected. The $^3A_{2g} \rightarrow {}^3T_{1g}$ transition at 527 nm is in good agreement, but we were unable to identify a band at 374 nm—instead, we observe a very intense charge-transfer band at 325 (14000) nm. Dq for $[Ni([9]aneS_3)_2]^{2+}$ is calculated to be 1276 cm^{-1} (B = 680 cm^{-1}), and for $[Ni([9]aneN_3)_2]^{2+}$ a value of 1250 cm^{-1} (B = 853 cm^{-1}) has been reported.[1] From these results it is concluded that 1,4,7-trithiacyclononane exerts a strong ligand field, which is slightly stronger than that of its nitrogen analogue 1,4,7-triazacyclononane. The LF strengths of these saturated N_3 and S_3 macrocycles are comparable with those of $[Ni(bpy)_3]^{2+}$ (Dq is found to be 1265 cm^{-1} [14]). $[Fe([9]aneS_3)_2]^{2+}$ is to the best of our knowledge the first example of an octahedral $Fe^{II}S_6$ complex with a low-spin d^6 electronic configuration.

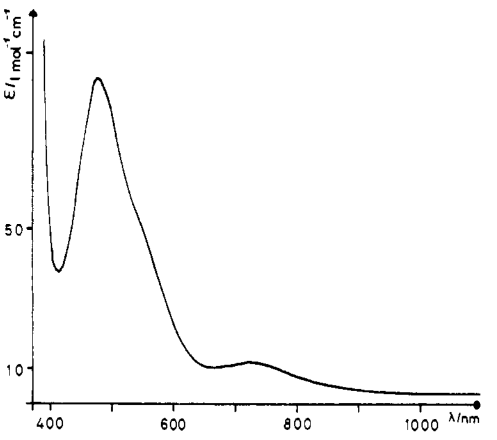

Figure 2. Electronic spectrum of $[Co([9]aneS_3)_2]^{2+}$ in acetonitrile.

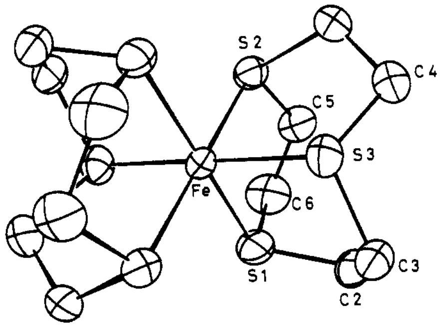

Figure 3. Molecular geometry and atomic labeling scheme of $[Fe([9]aneS_3)_2]^{2+}$.

Furthermore, the above conclusion is nicely corroborated by the observation that $[Co([9]aneS_3)_2]^{2+}$ is low-spin condition ($t_{2g}^6e_g^1$), whereas the $[Co([9]aneN_3)_2]^{2+}$ species is high-spin ($t_{2g}^5e_g^2$).[4] Consequently, the electronic spectra of these two complexes are very different (Table IV). Figure 2 shows the electronic spectrum of $[Co([9]aneS_3)_2](ClO_4)_2$ in acetonitrile,

---

(11) Wieghardt, K., unpublished results.

(12) Lever, A. B. P. "Inorganic Electronic Spectroscopy", 2nd ed.; Elsevier: Amsterdam, 1984; p 462 ff.

(13) Dabrowiak, J. C.; Merrell, P. H.; Busch, D. H. *Inorg. Chem.* **1972**, *9*, 1979.

(14) Jørgensen, C. K. *Adv. Chem. Phys.* **1963**, *5*, 33.

(15) Pignolet, L. H.; Lewis, R. A.; Holm, R. H. *J. Am. Chem. Soc.* **1971**, *93*, 360.

(16) (a) Cottrell, P. T.; Mann, C. K. J. *J. Electrochem. Soc.* **1969**, *116*, 1499. (b) Chamber, J. Q. In "Encyclopedia of Electrochemistry of the Elements"; Bard, A. J., Lund, H., Eds.; Marcel Dekker: New York, 1978; Organic Section, Vol. 12, p 329 ff. (c) Coleman, B. R.; Glass, R. S.; Setzer, W. N.; Prabhu, U. D. G.; Wilson, G. S. In "Electrochemical and Spectrochemical Studies of Biological Redox Components"; Kadish, K. M., Ed.; American Chemical Society: Washington, DC, 1982; Adv. Chem. Ser. No. 201, p 431.

(17) Larsen, E.; La Mar, G. N.; Wagner, B. E.; Parks, J. E.; Holm, R. H. *Inorg. Chem.* **1972**, *11*, 2652.

(18) Zhu, T.; Su, C. H.; Lemke, B. K.; Wilson, L. J.; Kadish, K. M. *Inorg. Chem.* **1983**, *22*, 2527.

(19) (a) Tanaka, N.; Sato, Y. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2059. (b) Fitzgerald, R. J.; Gutchinson, B. B.; Nakamoto, K. *Inorg. Chem.* **1970**, *9*, 2618. (c) Waind, G. M.; Martin, B. *J. Inorg. Nucl. Chem.* **1958**, *8*, 551. (d) Maki, N.; Yamagami, M.; Itatani, H. *J. Am. Chem. Soc.* **1964**, *86*, 114.

(20) Dubs, R. U.; Gahan, L. R.; Sargeson, A. M. *Inorg. Chem.* **1983**, *22*, 2523.

Table V. Electrochemical Data^e

compd	E^f, V^a	ΔE_p, mV^b	$I_{p,ox}/I_{p,red}$	
1,4,7-trithiacyclononane	+0.99^c			irrev
$Fe([9]aneS_3)_2^{2+}$	+0.98	70	1.06	rev
	−1.93^d			irrev
$Ni([9]aneS_3)_2^{2+}$	+0.97	80	1.2	quasi-rev
$Co([9]aneS_3)_2^{2+}$	−0.013	75	1.0	rev
	−0.86	70	1.05	rev

^{a} Formal redox potentials in volts vs. the reference system ferrocenium (Fc^+)/ferrocene (Fc). ^{b} Peak potential difference at a scan rate of 50 mV s^{-1}. ^{c} Oxidation potential at scan rate of 100 mV s^{-1}. ^{d} Reduction potential. ^{e} Cyclic voltammograms were measured in acetonitrile with 0.1 M TBA(PF_6) as supporting electrolyte and 10^{-3} M samples at 22 °C at a Pt-button working electrode.

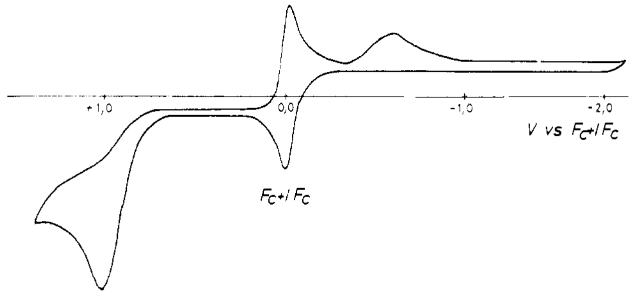

Figure 4. Cyclic voltammogram of 1,4,7-trithiacyclononane in acetonitrile at 22 °C (0.1 M TBA(PF_6) supporting electrolyte, 10^{-3} M ligand, and 10^{-3} M ferrocene as internal standard; Pt-button working electrode).

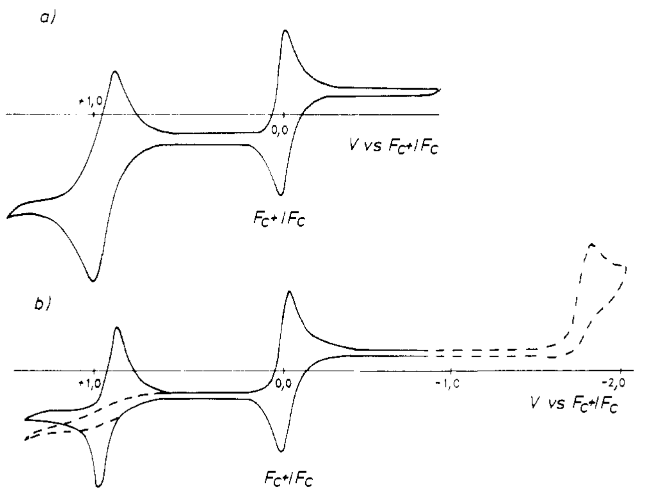

Figure 5. Cyclic voltammograms of (a) $[Ni([9]aneS_3)_2]^{2+}$ and (b) $[Fe([9]aneS_3)_2]^{2+}$ in acetonitrile at 22 °C (0.1 M TBA(PF_6) supporting electrolyte, 10^{-3} M complex, and 10^{-3} M ferrocene).

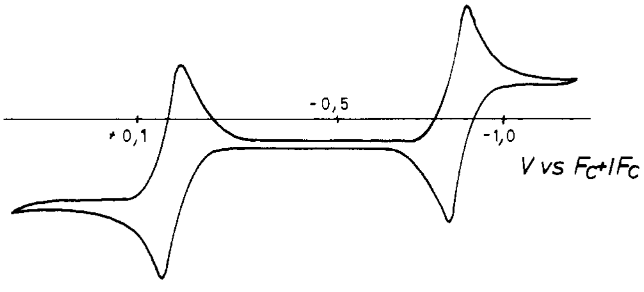

Figure 6. Cyclic voltammogram of $[Co([9]aneS_3)_2]^{2+}$ in acetonitrile at 22 °C (0.1 M TBA(PF_6) supporting electrolyte and 10^{-3} M complex).

which again does not agree with the reported spectrum measured in nitromethane.[6] The low-intensity band at 730 nm is assigned to the $^4T_{1g} \rightarrow {}^4T_{2g}$ and the shoulder at 560 nm to the $^4T_{1g} \rightarrow {}^4A_{2g}$ transitions. The band at 478 nm may then correspond to a $^4T_{1g} \rightarrow {}^4T_{1g}$ (P) transition. Similar spectra have been reported for low-spin $[Ni([9]aneN_3)_2]^{3+}$ [4] and $[Ni(dtne)]^{3+}$ (dtne = 1,2-bis(1,4,7-triaza-1-cyclononyl)ethane).[21]

It is noted that similar complexes of Co(II) and Ni(II) have been reported with the hexadentate crown thioether hexathio-18-crown-6.[22] The Co(II) complex is also low spin.

Crystal Structure. Crystals of $[Fe([9]aneS_3)_2](PF_6)_2$ consist of discrete, well-separated $[Fe([9]aneS_3)_2]^{2+}$ cations and PF_6^- anions. Figure 3 shows the molecular geometry and the atomic labeling scheme for $[Fe([9]aneS_3)_2]^{2+}$. Bond distances and angles are summarized in Table III. The metal atom occupies a crystallographic inversion center, which is in a nearly perfect octahedral environment of six sulfur atoms provided by two facially coordinating tridentate thioether ligands. The S–Fe–S angles average 90°; the average Fe–S distance is 2.250 Å. The average M–S bond distances in the cobalt, nickel, and copper analogues are 2.321, 2.386, and 2.422 (2.459) Å, respectively.[6] Glass et al.[6] have noted that "surprisingly the M–S bond lengths in these complexes increase in the order Co < Ni < Cu, whereas ionic radii increase in the order $Ni^{II} < Cu^{II} < Co^{II}$". Using ionic radii for octahedral complexes of low-spin Fe^{II}, low-spin Co^{II}, Ni^{II}, and Cu^{II}, which increase in this order, we find that the observed M–S bond order Fe < Co < Ni < Cu is in accord.[23]

Electrochemistry. Electrochemical data of complexes and of the uncoordinated ligand are summarized in Table V. The cyclic voltammogram of 1,4,7-trithiacyclononane in acetonitrile exhibits one irreversible oxidation peak at +0.99 V vs. Fe^+/Fc and an ill-defined reduction peak at −0.7 V (Figure 4). This behavior agrees well with the electrochemistry of other aliphatic thioethers in aprotic medium. The oxidation is usually a two-electron irreversible process and leads to the formation of sulfonium ions, sulfoxides, and various condensed species.[16]

The cyclic voltammograms of $[Fe([9]aneS_3)_2]^{2+}$, $[Ni([9]aneS_3)_2]^{2+}$, and $[Co([9]aneS_3)_2]^{2+}$ in acetonitrile are shown in Figures 5 and 6. In the potential range +1.5 to −2.0 V (vs. Fc^+/Fc) the cyclic voltammogram of $[Fe([9]aneS_3)_2]^{2+}$ shows a reversible one-electron-transfer process at $E_{1/2}$ = +0.982 V vs. Fc^+/Fc. The ratio $I_{p,ox}/I_{p,red}$ of unity and ΔE_p of 90 mV are nearly independent of the scan rate (10–500 mV s^{-1}). At very negative potentials an irreversible reduction is observed. Very similar behavior is observed for $[Ni([9]aneS_3)_2]^{2+}$: a quasi-reversible one-electron-transfer process occurs at $E_{1/2}$ = 0.97 V vs. Fc^+/Fc. It is noted that the oxidation potential of the uncoordinated ligand and the formal redox potentials of the above two complexes are nearly identical. This may indicate that the metal centers in the two complexes are *not* oxidized to the +III oxidation state but rather a reversible one-electron oxidation of the ligand occurs, generating a sulfonium ion coordinated to the metal(II) centers.

In contrast, the cyclic voltammogram of $[Co([9]aneS_3)_2]^{2+}$ (Figure 6) exhibits two reversible one-electron-transfer reactions at formal redox potentials of −0.013 and −0.86 V vs. Fc^+/Fc in the potential range of −1.5 to +0.5 V vs. Fc^+/Fc. The former is assigned to the couple $[Co^{III}([9]aneS_3)_2]^{3+}/[Co^{II}([9]aneS_3)_2]^{2+}$ whereas the latter corresponds to the couple Co(II)/Co(I). Thus reduction of Co(II) to Co(I) is observed:

$$[Co^{I}([9]aneS_3)_2]^+ \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [Co^{II}([9]aneS_3)_2]^{2+} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [Co^{III}([9]aneS_3)_2]^{3+}$$

Co(I) complexes in an octahedral environment of six nitrogens have in the past been generated electrochemically and chemically with use of unsaturated N-macrocycles[17,18] and 2,2′-bipyridine ligands.[19] $[Co([9]aneS_3)_2]^+$ appears to be the first example containing a set of saturated donor atoms with only a limited π-acceptor capability. The strong LF of 1,4,7-trithiacyclononane stabilizes the lower oxidation states of cobalt. On the other hand, the $[Co^{III}([9]aneS_3)_2]^{3+}$ species is a strong one-electron oxidant.

---

(21) Wieghardt, K.; Tolksdorf, I.; Herrmann, W. *Inorg. Chem.* **1985**, *24*, 1230.

(22) Hartmann, J. R.; Hintsa, E. J.; Cooper, S. R. *J. Chem. Soc., Chem. Commun.* **1984**, 386; *J. Am. Chem. Soc.* **1983**, *105*, 3738.

(23) Ionic radii were taken from: Huheey, J. E. In "Inorganic Chemistry: Principles of Structure and Reactivity", 3rd ed. (International Si Edition); Harper and Row: New York, 1983; p 73.

Similar observations have been made by Sargeson et al. for a low-spin Co(II) complex containing a saturated N_3S_3-donor set in an encapsulating caging ligand.[20]

Summary. Electronic spectra, effective magnetic moments, and crystallographic structure determinations of bis(1,4,7-trithiacyclononane)metal(II) complexes (M = Fe, Co, Ni, Cu) have convincingly shown that the small cyclic trithia crown ether is ideally suited to bind these metal centers in an octahedral environment of six sulfur atoms. The ligand exerts a slightly stronger LF than its nitrogen analogue 1,4,7-triazacyclononane, effecting low-spin d^6 and d^7 electronic configurations of Fe(II) and Co(II), respectively.

Acknowledgment. We thank the Fonds der Chemischen Industrie for financial support of this work.

Registry No. $[Ni([9]aneS_3)_2](BF_4)_2$, 83650-36-6; $[Co([9]aneS_3)_2](BF_4)_2$, 83650-38-8; $[Fe([9]aneS_3)_2](ClO_4)_2$, 97391-12-3; $Fe(ClO_4)_3\cdot 6H_2O$, 55144-08-6; $[Ni([9]aneS_3)_2](ClO_4)_2$, 97465-53-7; $[Co([9]aneS_3)_2](ClO_4)_2$, 97465-54-8; $[Fe([9]aneS_3)Cl_3]$, 97391-13-4; $[Fe([9]aneS_3)_2](PF_6)_2$, 97391-14-5; $[Co^I([9]aneS_3)_2]^+$, 97391-15-6; $[Co^{III}([9]aneS_3)_2]^{3+}$, 97391-16-7; $[9]aneS_3$, 6573-11-1.

Supplementary Material Available: Tables of thermal parameters, coordinates of calculated positions of H atoms, and observed and calculated structure factor amplitudes (17 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, Seattle Pacific University,
Seattle, Washington 98119, and University of Washington, Seattle, Washington 98195

Preparation and Raman Spectra of Thallium(I) Disulfite and Thallium(I) Sulfite

LYLE PETER* and BEAT MEYER

Received December 10, 1984

Thallium(I) disulfite, $Tl_2S_2O_5$, is the product of the reaction of TlOH and liquid sulfur dioxide. Its Raman spectrum closely resembles those of the alkali-metal disulfites. It slowly decomposes at room temperature to thallium(I) sulfite and sulfur dioxide. Comparisons of the vibrational spectra of the thallium(I) sulfite and disulfite with the infrared spectra of the argon-matrix reaction products of Tl_2O and sulfur dioxide indicate that these products are not simply the sulfite and disulfite, as was previously suggested, but that they are probably complex mixtures of several thallium–sulfur–oxygen compounds.

Introduction

Because of the international concern about "acid rain", and because of the diverse and interesting chemistry of sulfur compounds, the reaction chemistry of sulfur dioxide continues to have both practical and theoretical importance.[1] As an acidic oxide, it reacts readily with basic metallic oxides and hydroxides to form three series of salts. Under basic conditions, and with polyvalent cations, only compounds with sulfite (SO_3^{2-}) are produced.[2] With excess SO_2 and/or under acidic conditions, the aqueous solution contains equilibrium mixtures[3] of aquated SO_2, bisulfite with a protonated sulfur atom[3] (HSO_3^-), bisulfite with a protonated oxygen atom[4] (SO_3H^-), and disulfite ($S_2O_5^{2-}$). However, only salts of $S_2O_5^{2-}$ and HSO_3^- are known,[3] and these are formed with monovalent cations such as the alkali metals. From direct reactions of SO_2 with solid alkali-metal hydroxides or their aqueous solutions, one obtains[3] disulfites for Li, Na, or K and bisulfites for Rb or Cs. The Rb and Cs bisulfites can be further dehydrated to the disulfites. Because cation size seems to be a factor in whether a bisulfite or a disulfite will form, we decided to try a reaction between SO_2 and wet TlOH to see whether $TlHSO_3$ or $Tl_2S_2O_5$ is favored. The thallous ion is about the same size[5] as Rb^+, so one would expect the bisulfite. Although thallous sulfite has been known for some time, neither the bisulfite nor the disulfite has been reported in preparative amounts. Recently, David and Ault[6] have interpreted infrared spectra of the reaction products of matrxi-isolated Tl_2O and SO_2 to indicate that Tl_2SO_3 and $Tl_2S_2O_5$ were formed. We report here the preparation and Raman spectra of pure, solid $Tl_2S_2O_5$ and Tl_2SO_3 and compare their properties to those of the corresponding alkali-metal compounds and the data recently published by David and Ault.[6]

Table I. Raman Frequencies (cm^{-1}) of the $S_2O_5^{2-}$ Ion in Various Compounds and Infrared Frequencies Assigned to $Tl_2S_2O_5$ in Matrices

$K_2S_2O_5$	$Rb_2S_2O_5$	$Cs_2S_2O_5$	$Tl_2S_2O_5$	$Tl_2S_2O_5$ (IR) matrix[b]
217 m[a]	220 m	224 m	212 m	
244 vs	242 vs	240 vs	225 vs	
318 m	315 m	315 m	307 m	
434 s	432 s	435 s	423 s	435
515 w	519 w	519 w	504 w	495
557 w	545 w	545 w	533 w	595
	558 vw	558 vw	546 vw	657
643 vw	643 vw	643 vw		776
653 s	654 s	654 s	641 s	882
970 w	950 w	952 w	959 w	956, 973
1060 s	1047 s	1047 s	1033 s	1040
1088 m	1068 w	1071 w		1050
1178 m	1154 w	1155 w	1120 w	1089
1178 m	1188 w	1181 w	1157 w	1102

[a] Key (relative intensities): vw = very weak, w = weak, m = medium, s = strong, vs = very strong. [b] Reference 6.

Experimental Section

A few drops of water were added to wet some solid TlOH in a tube, which was fitted for a vacuum line. The slurry was degassed and SO_2 condensed onto it at 77 K. The system was allowed to warm to room temperature in a sealed pressure container, so that the SO_2 remained liquid. After several minutes, the excess SO_2 and water were evaporated on the vacuum line. The white residue was collected, and its Raman spectrum was recorded. The sample was stored in a vacuum for 24 h,

---

* To whom correspondence should be addressed at Seattle Pacific University.

(1) Meyer, B. "Sulfur Energy and Environment"; Elsevier: Amsterdam, 1977.

(2) Nickless, G. In "Inorganic Sulfur Chemistry"; Nickless, G., Ed.; Elsevier: Amsterdam, 1968; Chapter 14.

(3) (a) Meyer, B.; Peter, L.; Shaskey-Rosenlund, C. *Spectrochim. Acta, Part A* **1979**, *35A*, 345. (b) Peter, L. B. Ph.D. Dissertation, University of Washington, 1979; *diss. Abstr. Int. B.* **1980**, *40*, 5664.

(4) (a) Connick, R. E.; Tam, T. M.; Von Deuster, E. *Inorg. Chem.* **1982**, *21*, 103. (b) Connick, R. E.; Homes, D. A. "The Kinetics of Exchange between Bisulfite Ion and Water as Studied by Oxygen-17 NMR Spectroscopy", LBL Report-18297; Lawrence Berkeley Laboratory: Berkeley, CA, Aug 1984.

(5) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr. Struct., Crystallogr. Cryst. Chem.* **1969**, *B25*, 925.

(6) David, S. J.; Ault, B. S. *Inorg. Chem.* **1984**, *23*, 1211.

0020-1669/85/1324-3071$01.50/0