exhibit similar changes in the structurally sensitive meta proton region of the TMPP ligand. Detailed studies of these and other small molecule reactions will be published in due course.[18]

Acknowledgment. We are grateful to Michigan State University for support of this work and to Johnson Matthey for a generous loan of rhodium trichloride. X-ray equipment was supported by a grant from the National Science Foundation (CHE-8403823). We thank Laura Pence for the ORTEP diagram and Steven Haefner for help with the NMR experiments.

Supplementary Material Available: Tables of crystallographic data, atomic parameters, equivalent isotropic displacement parameters, bond distances, bond angles, and anisotropic thermal parameters (13 pages); a table of observed and calculated structure factors (35 pages). Ordering information is given on any current masthead page.

---

(18) Chen, S. J.; Dunbar, K. R. Unpublished results.

Department of Chemistry
Michigan State University
East Lansing, Michigan 48824

S. J. Chen
K. R. Dunbar*

Received September 21, 1989

Synthesis of $[Ru(CO)_2(Se_4)_2]^{2-}$. A Stable Anionic Ru^{2+} Polychalcogenide Complex

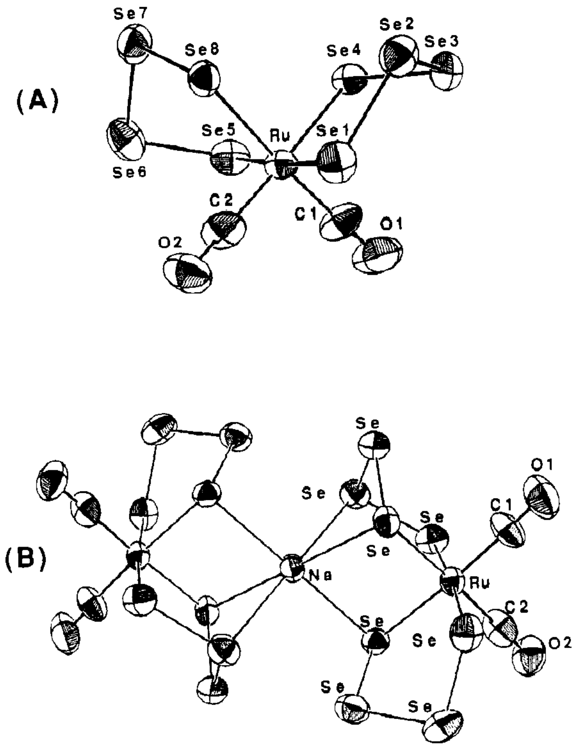

Figure 1. (A) ORTEP drawing of the $[Ru(CO)_2(Se_4)_2]^{2-}$ ion showing the labeling scheme. (B) Representation of the $[Na\{(Ru(CO)_2(Se_4)_2)\}_2]^{3-}$ portion of the structure showing the coordination environment of the Na^+ ion by two $[Ru(CO)_2(Se_4)_2]^{2-}$ ions. Selected bond distances (Å): Ru–C(1), 1.858 (8); Ru–C(2), 1.846 (8); Ru–Se(1), 2.517 (1); Ru–Se(4), 2.566 (1); Ru–Se(5), 2.513 (1); Ru–Se(8), 2.588 (1); Se(1)–Se(2), 2.346 (1); Se(2)–Se(3), 2.323 (1); Se(3)–Se(4), 2.353 (1); Se(5)–Se(6), 2.339 (1); Se(6)–Se(7), 2.315 (1); Se(7)–Se(8), 2.369 (1); C(1)–O(1), 1.132 (10); C(2)–O(2), 1.137 (10); Na–Se(2), 3.148 (1); Na–Se(4), 2.939 (1); Na–Se(8), 2.921 (1). Selected angles (deg): C(1)–Ru–C(2), 95.0 (2); Se(1)–Ru–Se(4), 97.32 (4); Se(1)–Ru–Se(5), 174.95 (5); Se(1)–Ru–Se(8), 79.45 (4); Se(4)–Ru–Se(5), 80.72 (4); Se(4)–Ru–Se(8), 93.58 (3); Se(5)–Ru–Se(8), 95.99 (4); Se(1)–Se(2)–Se(3), 99.25 (5); Se(2)–Se(3)–Se(4), 97.19 (5); Se(5)–Se(6)–Se(7), 99.64 (5); Se(6)–Se(7)–Se(8), 97.28 (5); C(1)–Ru–Se(1), 93.4 (2); C(1)–Ru–Se(4), 85.4 (2); C(1)–Ru–Se(5), 91.1 (2); C(1)–Ru–Se(8), 172.6 (2); C(2)–Ru–Se(1), 89.4 (2); C(2)–Ru–Se(4), 173.2 (2); C(2)–Ru–Se(5), 92.5 (2); C(2)–Ru–Se(8), 86.9 (2).

RuS_2 is one of the most active catalysts known for the hydrodesulfurization, HDS, of crude oil.[1,2] As with the other HDS catalysts (i.e. MoS_2, WS_2, and "CoMoS"), the mechanism of its action is currently unknown.[3] Although this challenge has driven the development of a great deal of Mo and W chemistry[4] with polysulfide ligands in an effort to find suitable model compounds for the surface of MoS_2, relatively little has been accomplished in the corresponding Ru/S chemistry. The Ru/S system has proven somewhat recalcitrant to study in the sense that, to date, no homoleptic Ru/S complexes have been isolated in pure form and/or structurally characterized. We are interested in the RuS_2/HDS problem from the standpoint of mimicking the active sites present in RuS_2. By exploring the fundamentals of Ru^{2+}/polychalcogenide chemistry, we aim to establish the currently unknown coordination preferences of this metal with HDS-relevant ligands. Thus far, the only Ru polychalcogenide complexes known are $[Ru(NH_3)_5]_2S_2^{4+}$,[5] $[CpRu(PR_3)_2]_2S_2^{2+}$,[6] $[MeCpRu(PPh_3)]_2S_x$ (x = 4, 6),[7] $Cp^*_2Ru_2(S_2)_2$,[8] $(Me_3P)_3RuS_7$,[9] $Ru(CO)_2(PPh_3)_2(S_2)$,[10] and $(bpy)_2RuS_5$, of which the last three have not been crystallographically characterized.[11] The only structurally characterized corresponding polyselenide complexes are the cationic $[CpRu(PPh_3)_2]_2Se_2^{2+}$ and $[MeCpRu(PPh_3)]_2(Se_2)_2^{2+}$.[12] The absence of homoleptic anionic Ru/Q_x (Q = S, Se, Te) complexes is probably due to their instability with respect to internal redox processes. Although Se ligands are not HDS-relevant, structures stabilized only by selenium ligands may emulate or represent difficult to isolate reactive intermediates in sulfur chemistry, and thus provide useful insight into the problem. We report here the synthesis and structural and spectroscopic characterization of the first stable anionic Ru/polyselenide complex, $[Ru(CO)_2(Se_4)_2]^{2-}$.

---

(1) (a) Chianelli, R. R.; Pecoraro, T. A.; Halbert, T. R.; Pan, W.-H.; Stiefel, E. I. *J. Catal.* **1984**, *86*, 226–230. (b) Pecoraro, T. A.; Chianelli, R. R. *J. Catal.* **1981**, *67*, 430–445.

(2) Harris, S.; Chianelli, R. R. *J. Catal.* **1984**, *86*, 400–412.

(3) (a) Derouane, E. G.; Pedersen, E.; Clausen, B. S.; Gabelica, Z.; Candia, R.; Topsoe, H. *J. Catal.* **1986**, *99*, 253–261. (b) Roberts, J. T.; Friend, C. M. *J. Am. Chem. Soc.* **1986**, *108*, 7204–7210.

(4) (a) Coucouvanis, D.; Toupadakis, A.; Koo, S.-M.; Hadjikyriacou, A. *Polyhedron* **1989**, *8*, 1705–1716. (b) Steifel, E. I.; Halbert, T. R.; Coyle, C. L.; Wei, L.; Pan, W.-H.; Ho, T. C.; Chianneli, R. R.; Daage, M. *Polyhedron* **1989**, *8*, 1625–1629. (c) Müller, A. *Polyhedron* **1986**, *5*, 323–340. (d) Pan, W. H.; Leonowicz, M. E.; Stiefel, E. I. *Inorg. Chem.* **1983**, *22*, 672–678. (e) Coucouvanis, D.; Hadjikyriacou, A.; Draganjac, M.; Kanatzidis, M. G.; Ileperuma, O. *Polyhedron* **1986**, *5*, 349–356. (f) Coucouvanis, D.; Hadjikyriacou, A. *Inorg. Chem.* **1986**, *25*, 4317–4319. (g) Muller, K. R.; Bruce, A. E.; Corbin, J. L.; Wherland, S.; Stiefel, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 5102–5104. (h) Laurie, J. C. V.; Duncan, L.; Haltiwanger, R. C.; Weberg, R. T.; Rakowski-DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 6234–6241. (i) Weberg, R. T.; Haltiwanger, R. C.; Laurie, J. C. V.; Rakowski-DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 6242–6250. (j) Secheresse, F.; Lefebvre, J.; Daran, J. C.; Jeannin, Y. *Inorg. Chem.* **1982**, *21*, 1311–1314. (k) Cohen, S. A.; Stiefel, E. I. *Inorg. Chem.* **1985**, *24*, 4657–4662.

(5) (a) Brulet, C. R.; Isied, S. S.; Taube, H. *J. Am. Chem. Soc.* **1973**, *95*, 4758–4759. (b) Elder, R. C.; Trkula, M. *Inorg. Chem.* **1977**, *16*, 1048–1051.

(6) Amarasekera, J.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1987**, *26*, 3328–3332.

(7) Amarasekera, J.; Rauchfuss, T. B.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 2017–2018.

(8) Rauchfuss, T. B.; Rodgers, D. P. S.; Wilson, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 3114–3115.

(9) Gotzig, J.; Rheingold, A. L.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 814–815.

(10) (a) Clark, G. R.; Russell, D. R.; Roper, W. R.; Walker, A. *J. Organomet. Chem.* **1977**, *136*, C1–C3. (b) Farrar, D. H.; Grundy, K. R.; Payne, N. C.; Roper, W. R.; Walker, A. *J. Am. Chem. Soc.* **1979**, *101*, 6577–6582.

(11) Greaney, M. A.; Coyle, C. L.; Harmer, M. A.; Jordan, A.; Stiefel, E. I. *Inorg. Chem.* **1989**, *28*, 912–920.

(12) Amarasekera, J. Ph.D. Thesis. University of Illinois, 1988.

0020-1669/90/1329-0590$02.50/0

$Ru_3(CO)_{12}$ reacts with a solution of Na_2Se_5 and Et_4NCl in acetone in a 1:6:6 molar ratio within several hours. Filtration of the resulting brown solution and dilution with ether yield crystalline, air-sensitive red-orange $(Et_4N)_{1.5}Na_{0.50}[Ru(CO)_2(Se_4)_2]$ (I) in 70% yield. It is important that the solution of $Ru_3(CO)_{12}$ is added dropwise to the solution of Na_2Se_5.[13] Crystals of I suitable for X-ray diffraction were obtained and subjected to a crystal structure determination.[14] The product is homogeneous, giving an X-ray powder diffraction pattern identical with that calculated from single-crystal data.[15]

The crystal structure of $(Et_4N)_{1.5}Na_{0.50}[Ru(CO)_2(Se_4)_2]$ consists of noninteracting Et_4N^+ cations and interacting Na^+ and $[Ru(CO)_2(Se_4)_2]^{2-}$ ions. $[Ru(CO)_2(Se_4)_2]^{2-}$ adopts an octahedral geometry with two cis CO groups and two chelating Se_4^{2-} ligands, as shown in Figure 1A. The molecule possesses a noncrystallographic 2-fold axis that bisects the C(1)–Ru–C(2) and Se(4)–Ru–Se(8) angles. The Ru–C(1) and Ru–C(2) bond distances are 1.858 (7) and 1.846 (7) Å, respectively, with a C(1)–Ru–C(2) angle of 95.0 (2)°. The Ru–Se bonds are divided into two sets of short and long bonds. The Ru–Se(1) and Ru–Se(5) bonds are trans to each other at 2.517 (1) and 2.513 (1) Å and are shorter than the corresponding cis Ru–Se(4) and Ru–Se(8) bonds at 2.566 (1) and 2.588 (1) Å, respectively. The lengthening of the Ru–Se bonds that are disposed trans to the carbonyl groups reflects the effective competition between the latter and the Se_4^{2-} ligands for both σ (xy orbital) and to a lesser extent π (xz and yz orbitals) bonding to the metal center. The Se_4^{2-} ligands adopt both half-boat (Se(1)/Se(2)/Se(3)/Se(4)) and envelope (Se(5)/Se(6)/Se(7)/Se(8)) conformations. Selected bond distances and angles are given in the caption of Figure 1. In both Se_4^{2-} ligands there is an alternation of a long Se(external)–Se(internal) average of 2.352 (11) Å and a short Se(internal)–Se(internal) average of 2.319 (4) Å. A similar Se–Se bond alternation was observed in $[Zn(Se_4)_2]^{2-}$.[16]

The Na^+ ion is important in the crystallization of I. The use of K_2Se_5 as a reagent in the synthesis of this complex resulted only in a poorly crystalline powder which did not contain K^+. The Na^+ ion is found in a center of symmetry (0, $^1/_2$, 0), and it is coordinated by two centrosymmetrically disposed $[Ru(CO)_2(Se_4)_2]^{2-}$ anions through the Se(2), Se(4), and Se(8) atoms, as shown in Figure 1B. The Se atoms create an excellent octahedral pocket for Na^+. The Na- - -Se distances range from 2.921 (1) to 3.148 (1) Å.

In solution, the diamagnetic $[Ru(CO)_2(Se_4)_2]^{2-}$ ion maintains its integrity, but it is no longer associated with the Na^+ ion. The UV/vis spectrum in DMF is a featureless rising absorbance. The ^{13}C NMR spectrum of $[Ru(CO)_2(Se_4)_2]^{2-}$ in DMSO-d_6 shows one resonance at 199 ppm, assigned to the carbonyl carbon atom, as expected for a species of C_2 symmetry (a C_2 axis passes through the Ru atom, bisecting the C–Ru–C angle). Consistent with the C_2 point group symmetry, four resonances are observed in the ^{77}Se NMR spectrum respectively at 717, 650, 630, and 395 ppm (vs Me_2Se). The selenium atoms within the equivalent Se_4^{2-} ligands are in chemically different environments depending on how they are disposed relative to the CO ligands. Since we could not observe satellite peaks from either the Ru or the Se isotopes in the spectra, we are unable to assign unequivocally these resonances at this time. In the IR spectrum of I (KBr pellet), the symmetric and antisymmetric CO stretching vibrations occur at 1992 and 1927 cm^{-1}, respectively.

The high-yield synthesis of I should allow for a convenient entry into the elusive Ru/polychalcogenide chemistry. The use of I as a starting material for the synthesis of other Ru/Se complexes, a study of its chemical reactivity, and extension of this work to analogous polysulfide chemistry are in progress.

Acknowledgment. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Center for Fundamental Materials Research (CFMR) at Michigan State University, and the NSF (for a Presidential Young Investigator Award) is gratefully acknowledged.

Supplementary Material Available: Tables of atomic coordinates of all atoms and anisotropic and isotropic thermal parameters of all nonhydrogen atoms and tables of distances and angles (7 pages); a listing of calculated and observed ($10F_o/10F_c$) structure factors (27 pages). Ordering information is given on any current masthead page.

Department of Chemistry
Michigan State University
East Lansing, Michigan 48824-1322

M. Draganjac[17]
Sandeep Dhingra
Song-Ping Huang
Mercouri G. Kanatzidis*

Received October 12, 1989

---

(13) Na_2Se_5 was prepared from the reaction of the stoichiometric amounts of Na and Se in liquid ammonia.

(14) Crystal data for $(Et_4N)_{1.5}Na_{0.50}[Ru(CO)_2(Se_4)_2]$ (I): triclinic $P\bar{1}$, $Z = 2$, $a = 10.986$ (3) Å, $b = 10.979$ (2) Å, $c = 13.876$ (4) Å, $\alpha = 102.12$ (2)°, $\beta = 104.09$ (1)°, $\gamma = 113.33$ (1)°, $V = 1399.61$ Å^3 at 25 °C. $2\theta_{max}$(Mo Kα) = 48.3°; $D_{calc} = 2.43$ g/cm^3; number of data measured 4685; number of unique data 4472; number of data having $F_o^2 > 3\sigma(F_o^2)$ 2821; number of variables 240; number of atoms 35 (including disordered atoms). No crystal decay was observed. An empirical absorption correction was applied; $\mu = 110.3$ cm^{-1}. There are two crystallographically independent Et_4N^+ ions situated in a general position and an inversion center (0, 0, $^1/_2$), respectively. The minimum and maximum corrections were 0.40 and 0.99, respectively. Final $R = 0.054$ and $R_w = 0.061$.

(15) Smith, D. K.; Nichols, M. C.; Zolensky, M. E. *POWD 10: A FORTRAN Program for Calculating X-ray Powder Diffraction Patterns*, Version 10; The Pennsylvania State University: University Park, PA, 1983.

(16) Adel, J.; Weller, F.; Dehnicke, K. *Z. Naturforsch.* **1988**, *43B*, 1094–1100.

(17) Permanent address: Department of Chemistry, Arkansas State University, State University, AR 72467. 1989 ACS-PRF Summer Fellow.