Canadian Mineralogist
Vol. 16, pp. 447-452 (1978)

COVALENT CHEMICAL BONDING OF TRANSITION METALS IN PYRITE, COBALTITE, SKUTTERUDITE, MILLERITE AND RELATED MINERALS

LINUS PAULING[*]
Linus Pauling Institute of Science and Medicine
2700 Sand Hill Road, Menlo Park, California 94025, U.S.A.

ABSTRACT

Atoms of transition metals can form nine sp^3d^5 covalent bonds, either the neutral atoms (Co, Rh, Ir) or after addition of electrons (one added electron for Fe, Ru, Os). Structures involving enneacovalent iron and cobalt are described for pyrite, cobaltite and skutterudite. These structures are compatible with the electroneutrality principle when the partial ionic character of covalent bonds is taken into consideration. The structure assigned to millerite involves octacovalent nickel forming two single bonds with other nickel atoms and a resonating double bond and four single bonds with sulfur atoms. An explanation based on covalence and the electroneutrality principle is proposed for the observed geochemical distribution of metals between sulfide and silicate phases.

SOMMAIRE

Les atomes de métaux de transition peuvent former neuf liaisons covalentes de type sp^3d^5, soit comme atomes neutres (Co, Rh, Ir), soit après l'addition d'électrons (un électron supplémentaire pour Fe, Ru, Os). Des structures comportant du fer et du cobalt ennéacovalents sont décrites pour la pyrite, la cobaltite et la skutterudite. Ces structures sont compatibles avec le principe d'électroneutralité lorsque le caractère ionique partiel de liaisons covalentes est pris en considération. La structure attribuée à la millérite implique du nickel octacovalent formant deux liaisons simples avec d'autres atomes de nickel, une double liaison résonante et quatre liaisons simples avec des atomes de soufre. On propose une explication de la distribution géochimique observée de métaux entre les phases sulfure et silicate basée sur la covalence et sur le principe d'électroneutralité.

BOND ORBITALS OF TRANSITION-METAL ATOMS

The outer shell of transition metals contains nine orbitals: $4s\,4p^3\,3d^5$ for the iron sequence, $5s\,5p^3\,4d^5$ for the palladium sequence and $6s\,6p^3\,5d^5$ for the platinum sequence. It has been recently recognized that these orbitals can be hydridized into sets of nine good bond orbitals (McClure 1970; Pauling 1975a, b). The best sets of nine bond orbitals are the McClure set, the tetragonal antiprism with one cap, and the trigonal prism with caps on the three prismatic faces.

In a discussion of the structure of molecules and crystals an important basic principle, that of electroneutrality, has great value (Pauling 1960). According to this principle, stable structures are those in which each atom has an electric charge close to zero, the limits being -1 and $+1$. The electric charge is the resultant of electron transfer and the partial ionic character of the covalent bonds formed by the atom.

The first assignment of a large value of the covalence to a transition-metal atom was made by Langmuir (1921) nearly sixty years ago. Nickel tetracarbonyl might be assigned a structure in which the nickel atom has five unshared electron pairs in its outer shell and forms single bonds with the four carbonyl groups, Ni–C≡O:$^{+}$. The formal charge $+1$ on each oxygen atom is partly neutralized by the ionic character (66% for the three bent single bonds) of the carbon–oxygen triple bond, and is hence acceptable for the carbonyl group; however, the formal charge of -4 for nickel, changed to only -3.7 by the partial ionic character of the nickel–carbon bonds, is not acceptable. Langmuir pointed out that the structure involving one unshared pair on the nickel atom and four nickel-carbon double bonds (Ni = C = Ö:) places zero formal charges on each atom and conforms to the electroneutrality principle. Verification of the structure was provided by the electron–diffraction study of Brockway & Cross (1935), who found the nickel–carbon

---

[*] José Donnay has worked in several fields of science that have also interested me. One of these fields is the structure of sulfide minerals, including chalcopyrite, andorite, sundtite, digenite and bornite. I am glad to present in the following pages a discussion of chemical bonding in some sulfide and arsenide minerals, written in honor of José Donnay.

distance to be 1.82 Å, the double-bond distance.

A striking example of enneacovalence (formation of nine covalent bonds) is that of the rhenium atom in the anion $[ReH_9]^{2-}$. Rhenium has seven valence electrons, and two others are provided by electron transfer from potassium atoms in the salt K_2ReH_9. The nine hydrogen atoms lie at the corners of a trigonal prism with three lateral caps (Abrahams *et al.* 1964), with a Re–H bond length of 1.68 Å, close to the expected value 1.69 Å for a single covalent bond (Pauling 1978c).

Enneacovalence is achieved by an iron atom by the transfer of an electron to it, either by a singly-bonded carbonyl or similar group (as in $Fe(CO)_5$, with one singly-bonded and four doubly-bonded carbonyls) or by formation of a negative ion, as in the compound $[\{(C_6H_5)_3P\}_2N]^+[HFe(CO)_4]^-$. In the $[HFe(CO)_4]^-$ ion the ion atom forms a single bond with the hydrogen atom and a double bond with each of the four carbonyl groups. Scores of molecules containing enneacovalent iron are known (see Pauling 1978a, b).

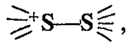
ENNEACOVALENT RADII

A set of values of enneacovalent radii of transition metals has been formulated (Pauling 1975a). The values are given in Table 1.

THE STRUCTURE OF PYRITE

Pyrite, FeS_2, was the first crystal with a variable atomic parameter to have its structure determined. Bragg in 1914 determined the value of the cell edge and obtained a rough value of the sulfur parameter. Several other early determinations of this parameter gave values in the range 2.05 Å to 2.14 Å for the S–S bond length, and in 1934 Huggins and I, in our discussion of tetrahedral covalent radii, accepted the value 2.08 Å for the sulfur–sulfur tetrahedral bond length (Pauling & Huggins 1934).

The electronic structure that we and others had accepted for pyrite is one in which (1) each sulfur atom forms four sp^3 single bonds, with the sulfur atom and three iron atoms that surround it at the corners of an approximately regular tetrahedron; (2) each iron atom forms six sp^3d^2 single bonds with the six sulfur atoms that surround it at the corners of an approximately regular octahedron. The structure is satisfactory in that the iron atom, with six shared electron pairs and three unshared pairs, has the krypton structure and the sulfur atom, with four shared pairs, has the argon structure. This structure, however, is now seen to be unacceptable, for two reasons. Firstly, it is in pronounced contradiction with the electroneutrality principle. The formal charge of the iron atom is −4 and that of each sulfur atom is +2, and these values are changed only to −3.3 and +1.65 by the ionic character of the bonds, as calculated from the electronegativity values 1.8 for Fe and 2.5 for S. Moreover, the observed S–S bond length in pyrite is not 2.08 Å, as indicated in the early studies, but about 2.17 Å, which corresponds to a transargononic structure for sulfur. I conclude accordingly that pyrite has a different structure, with enneacovalent iron and transargononic sulfur with average covalence 5.5.

Enneacovalent iron, Fe^-, results from the transfer of one electron to the iron atom from the disulfide group. The enneacovalent iron atom would form three single bonds and three double bonds with the six surrounding sulfur atoms. These bonds might resonate equally among the six positions, making them equivalent (bond number 1.5), as in the usually assigned cubic structure, space group T_h^6-$Pa3$. The S_2^+ group would then have the transargononic structure , with resonance to , and average covalence of each sulfur atom 5.5 (Pauling 1970).

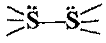
With nine covalent bonds having 12% ionic character, as given by the electronegativity difference, the charge on the iron atom is changed from the formal value −1 to +0.08, in excellent agreement with the electroneutrality principle. (In an earlier discussion of pyrite (Pauling 1970) I suggested another structure, involving transargononic sulfur, , and hexacovalent iron with one unshared pair. Since then the evidence about enneacovalent iron has become so strong as to make it likely that increased stability is in fact conferred on pyrite and other minerals by the use of all nine sp^3d^5 orbitals by the transition metals instead of only the seven used in this earlier structure.)

TABLE 1. SINGLE-BOND RADII (IN Å) FOR TRANSITION METALS WITH COVALENCE 9

Cr 1.26	Mn 1.25	Fe 1.24	Co 1.23	Ni 1.22
Mo 1.39	Tc 1.38	Ru 1.37	Rh 1.36	Pd 1.35
W 1.40	Re 1.39	Os 1.38	Ir 1.37	Pt 1.36

A careful high-resolution X-ray study of the electron-density distribution in pyrite by Stevens & Coppens (1978) has shown 8 peaks with difference heights 1.3 eÅ^3 at 0.6Å from the iron atom in the directions of the faces of the octahedron of sulfur atoms. The investigators point out that these maxima correspond to nonbonding electron pairs in d orbitals. For nine pure sp^3d^5 orbitals the electron distribution about the iron atom would be spherically symmetrical. I have pointed out, however, that for the quadrivalent carbon atom in methane quantum mechanical calculations show that the structure with four pure sp^3 covalent bonds contributes only 60% to the wave function for the ground state of the molecule, with the other 40% corresponding to structures with an unshared 2s electron pair on the carbon atom (Pauling 1960, p. 118-120, 414-416). Nevertheless, it is conventional to describe the carbon atom in methane as quadricovalent. In the same way, the enneacovalent iron atom in pyrite resonates between the pure enneacovalent structure and other structures involving one or more unshared electron pairs. A careful analysis of the electron distribution would reveal the extent of this resonance. A rough estimate is 0.63 unshared pairs on the iron atom, made with the assumption that a covalent bond has the same chance of putting an unshared pair on the iron atom as its partial ionic character (12%), and with consideration only of individual structures that place the formal charge +1, 0, or −1 on the iron atom.

In a study of transargonomic sulfur (Pauling 1970) I quoted the value 2.21 Å for S–S in F_5S–SF_5 and nearly equal values for several related compounds, and suggested the values 1.10 Å for the covalent radius for sulfur forming six sp^3d^2 covalent bonds and 1.07 Å for sulfur (S^+) forming five sp^3d covalent bonds. The sum of these values, 2.17 Å, would be expected in pyrite. Recent experimental values are 2.171 Å (Elliott 1960), 2.177 Å (Brostigen & Kjekshus 1969), and 2.14 to 2.17 Å (Bayliss 1977). For the marcasite form of FeS_2 the values 2.210 Å and 2.223 Å have been reported (Buerger 1937, Brostigen & Kjekshus 1969). For the pyrite-structure disulfides of ruthenium and osmium, the congeners of iron, the reported values are 2.179 Å and 2.210 Å, respectively (Sutarno *et al.* 1967). The average of these values, 2.189 Å, supports the assignment of covalent radius 1.10 Å to sexacovalent sulfur and a somewhat smaller value, perhaps 1.08 Å, to quinquecovalent sulfur.

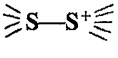
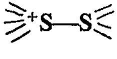
The observed iron–sulfur distance in pyrite is 2.26 Å, somewhat smaller than the sum of the single-bond radii, 2.34 Å. The correction for $n = 1.5$ given by the term -0.60 Å log n is -0.08 Å, which leads to agreement with observation.

COMPARISON WITH OTHER DISULFIDES

MnS_2, with one electron less than FeS_2, cannot form the full complement of nine bonds between the metal atom and the sulfur atom because of the deficiency of one electron. Moreover, CoS_2 and NiS_2, with one and two excess electrons, cannot form this full complement because one of the orbitals is occupied by the excess electron or electron pair. Accordingly we conclude that FeS_2 should be the most stable of the pyrite-type disulfides, and hence, that the lattice constant (edge of the unit cell) should be a minimum at FeS_2. This is borne out by experiment: the values for MnS_2, FeS_2, CoS_2 and NiS_2 are 6.095 Å, 5.404 Å, 5.523 Å and 5.677 Å. Similarly, the values for RuS_2 and RhS_2 are 5.610 Å and 5.574 Å, respectively; those for TcS_2 and PdS_2 are not known.

ANISOTROPIC PYRITE

Several investigators (quoted by Bayliss 1977) have noted that many samples of pyrite are weakly anisotropic. Bayliss made a careful X-ray examination of a weakly anisotropic pyrite sample from the Itaya mine, Yamagata Prefecture, Japan. The sample was analyzed by electron microprobe, and no deviation from the formula FeS_2 was found, the limits of detection of impurities (in weight percent) being Co 0.07, Ni 0.05, As 0.05, and Sb 0.03. The unit of structure was found to be isometric, with edge 5.417 Å, but many reflections not allowed by the ideal pyrite structure were observed; these reflections require the triclinic space group $P1$. The 36 positional parameters were determined. They correspond to Fe–S distances ranging from 2.23 Å to 2.30 Å, *i.e.*, to values of n from 1.2 to 1.7. The structure is similar to that of gersdorffite, Ni(As,S)$_2$ (Bayliss 1968, Bayliss & Stephenson 1968).

Bayliss points out that ordering of two kinds of atoms (As and S in gersdorffite) could cause the observed distortion, but that there is no chemical reason to cause such a shift in pyrite. In fact, the foregoing considerations do suggest a chemical reason. There are two possible structures of pyrite. In the high-temperature form the disulfide group might resonate completely between the two structures  and , with the sulfur atoms equivalent and the iron–sulfur bonds all equivalent. The crystal would then have the cubic *Pa*3 structure. The low-temperature structure would result from the inhibition of the resonance, so that the two sulfur atoms in each S_2^+ group would be dissimilar, and a deformed structure of the crystal would result. The S^+ atom, with four bonds to the three adjacent iron atoms, would form Fe–S bonds with n +1.333, bond length about 2.28 Å; the S atom, with five bonds to its iron neighbors, would form bonds with $n = 1.667$, bond length 2.22 Å.

COBALTITE

The neutral cobalt atom, with nine orbitals and nine valence electrons, can form nine covalent bonds. The $\geqq\mathrm{As}\text{—}\mathrm{S}\leqq$ group, with a transargononic structure for both arsenic and sulfur, can also form nine bonds. Accordingly the structure described for pyrite, but without electron transfer, is expected. The observed As–S distance (Giese & Kerr 1965), 2.32 Å, is 0.07 Å larger than the sum of the single-bond radii, reflecting the transargononic character of the atoms.

SKUTTERUDITE

In skutterudite, $CoAs_3$ or, better, $Co_4(As_4)_3$, there are square As_4 groups, with As–As bond length 2.52 Å (Mandel & Donohue 1971). This value is 0.10 Å larger than the normal-valence single-bond length, indicating transargononic character of arsenic. Three As_4 groups thus can form 36 bonds with cobalt, enough for the four enneacovalent cobalt atoms. No electron transfer is needed for enneacovalence of cobalt, and the electronegativity of arsenic, 2.0, is so close to that of cobalt, 1.9, that the bonds have very little ionic character, about 1%; hence, the electroneutrality rule is well satisfied. The stability of the mineral is accordingly explained by the structure.

OTHER SULFIDES AND ARSENIDES

Values of electronegativity (which depend to some extent on the valence state) are Cr 1.6, Mn 1.7, Fe 1.8, Co 1.9, Ni 1.9. Enneacovalent cobalt requires no electron transfer, and its compounds with atoms of nearly the same electronegativity, such as As (2.0) and Sb (1.9), should be the most stable. For enneacovalent manganese, Mn^{2-}, electroneutrality would result if the nine bonds were formed with atoms with electronegativity 2.7, somewhat larger than that of sulfur, 2.5. It is understandable that hauerite, MnS_2, and alabandite, MnS, as well as $MnSe_2$ and $MnTe_2$, involve manganese atoms with five unpaired electrons and with a small covalence (Elliott 1960). The observed S–S bond length in MnS_2 is 2.086Å (Offner 1934), which corresponds to an argononic structure.

Enneacovalence or octacovalence of manganese and chromium and their congeners is, however, exhibited in some of their compounds with oxygen. For example, scheelite, $CaWO_4$, a principal ore of tungsten, may be described as containing the ion WO_4^{2-}. The two electrons transferred to this ion suffice to make the tungsten atom octacovalent, permitting it to form a double bond with each of the four oxygen atoms. In fact, it can become enneacovalent by forming a triple bond, $W{\equiv}O{:}^+$, with one of them. Electroneutrality of tungsten would result if each of the nine bonds had 33% ionic character. This value is compatible with the somewhat uncertain value of the electronegativity of tungsten.

MILLERITE

Two independent structure determinations, agreeing very closely with one another, have recently been made of the rhombohedral mineral millerite, NiS (Grice & Ferguson 1974, Rajamani & Prewitt 1974). In this crystal each nickel atom has three sulfur atoms at 2.263 Å and two at 2.376 Å and two nickel atoms at 2.535 Å (average of values agreeing within 0.014 Å). It is evident that there are at least five covalent Ni–S bonds, because the calculated single-bond distance, using 1.10 Å for the radius of transargononic sulfur, is 2.32 Å. Moreover, each nickel atom forms two bonds with adjacent nickel atoms: the observed Ni–Ni distance 2.535 Å is a little larger than the single-bond value, 2.44 Å, calculated with the enneacovalent radius. There are two structures compatible with the electroneutrality principle. If no electron transfer takes place, the nickel atom, with an unshared pair occupying one its nine sp^3d^5 orbitals, can form eight bonds and the sulfur atom can form six bonds. Thus there would be two nickel–nickel single bonds and six nickel–sulfur single bonds (or, rather, one double bond and four single bonds) formed by each nickel atom. If the double bond resonates among the positions to the three nearer sulfur atoms their bond lengths would be shortened by 0.075 Å (that is, by 0.60 Å × log 4/3), giving the calculated value 2.245 Å for these bond lengths, in good agreement with the observed value 2.263 Å.

The difference in electronegativity values of Ni and S, 0.6, corresponds to 9% ionic character, which places the charge +0.54 on the nickel atom. With the alternative structure, involving transfer of an electron from S to Ni, the S^+ atom can form only five single bonds and the resultant charge on the nickel atom is −0.55. The two structures are thus equivalent with respect to electroneutrality, but the second one, in which nickel has two unshared pairs and can form only seven bonds, is less satisfactory than the first, which is stabilized by one more nickel–sulfur covalent bond. Both of these structures involve only shared or unshared electron pairs and hence correspond to diamagnetism or small temperature-independent paramagnetism. I conclude that the nickel atom in millerite is octacovalent.

GEOCHEMISTRY OF THE TRANSITION METALS

We may expect in general that the stability of a compound with a transition metal is great if all or most of the nine sp^3d^5 orbitals are used in bond formation. The principal atoms ligated by these metals in nature are sulfur, with electronegativity 2.5, and oxygen, with electronegativity 3.5. Cobalt, rhodium and iridium, with nine valence electrons in the neutral atom and electronegativity 1.9 to 2.2, cannot form nine stable bonds with oxygen because the large amount of ionic character, 40 to 50%, would place too much positive charge on the enneacovalent atom; however, they can form nine stable bonds with sulfur. On the other hand, chromium, molybdenum and tungsten, with nine valence electrons after transfer of three to give Cr^{3-}, Mo^{3-}, and W^{3-}, and with electronegativity 1.6 to 1.8, cannot form nine stable bonds with sulfur but can form them with oxygen, the bonds with oxygen having enough ionic character to neutralize the formal charge. We expect accordingly that the metals Co, Rh, Ir and those adjacent to them will be concentrated in sulfide deposits, whereas the others will be concentrated in rocks (silicates and oxides). Reference to tabulations (as in Smithells 1949) shows that the ratio of weight percentage in sulfides to weight percentage in rocks is Fe 10.8, Co 100, Ni 400, Cu 150 and Zn 100, which may be compared with V 0.25, Cr 0.0001 and Mn 0.8. Values greater than 1 for this ratio are found also for Mo, Ru, Rh, Pd, Ag, Cd, In and for W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb. The stability of the sulfides of the group VIII transition metals has in the past constituted a puzzle, in that stability for most compounds is associated with a large difference in electronegativity of the bonded atoms and consequent large amount of ionic character of the bonds, giving a large amount of ionic-covalent resonance energy. The solution to the puzzle is that for the transition metals an important factor determining the stability is the extent to which the nine sp^3d^5 orbitals can be used in the formation of bonds. Enneacovalence of transition-metal atoms explains why ore minerals such as FeS_2, CoAsS, $CoAs_3$, RuS_2 and OsS_2 have wide occurrence.

Many other compounds are known in which the transition metal is enneacovalent: $FeSe_2$, $FeTe_2$, RuS_2, $RuSe_2$, $RuTe_2$, OsS_2, $OsSe_2$ and $OsTe_2$ have either the pyrite or the marcasite structure, and CoP_3, $CoSb_3$, RhP_3, $RhSb_3$, IrP_3 and $IrSb_3$ have the skutterudite structure. The crystals have the expected properties, such as the transargononic values of the X–X bond lengths and lattice constants less than for similar crystals with more or fewer electrons.

REFERENCES

ABRAHAMS, S. C., GINSBERG, A. P. & KNOX, K. (1964): Transition metal-hydrogen compounds. II. The crystal and molecular structure of potassium rhenium hydride, K_2ReH_9. *Inorg. Chem.* **3**, 558-567.

BAYLISS, P. (1968): The crystal structure of disordered gersdorffite. *Amer. Mineral.* **53**, 290-293.

——— (1977): Crystal structure refinement of a weakly anisotropic pyrite. *Amer. Mineral.* **62**, 1168-1172.

——— & STEPHENSON, N. C. (1968): The crystal structure of gersdorffite (III), a distorted and disordered pyrite structure. *Mineral. Mag.* **36**, 940-947.

BRAGG, W. L. (1914): The analysis of crystals by the X-ray spectrometer. *Proc. Roy. Soc. London* **A89**, 468-489.

BROCKWAY, L. O. & CROSS, P. C. (1935): The molecular structure of nickel carbonyl. *J. Chem. Phys.* **3**, 828-833.

BROSTIGEN, G. & KJEKSHUS, A. (1969): Redetermined crystal structure of FeS_2 (pyrite). *Acta Chem. Scand.* **23**, 2186-2188.

BUERGER, M. J. (1937): Interatomic distances in marcasite and notes on the bonding in crystals of löllingite, arsenopyrite, and marcasite types. *Z. Krist.* **97**, 504-513.

ELLIOTT, N. (1960): Interatomic distances in FeS_2, CoS_2, and NiS_2. *J. Chem. Phys.* **33**, 903-905.

GIESE, R. F., JR. & KERR, P. F. (1965): The crystal structures of ordered and disordered cobaltite. *Amer. Mineral.* **50**, 1002-1014.

GRICE, J. D. & FERGUSON R. B. (1974): Crystal structure refinement of millerite (β-NiS). *Can. Mineral.* 12, 248-252.

LANGMUIR, I. (1921): Types of valence. *Science* 54, 59-67.

MANDEL, N. & DONOHUE, J. (1971): The refinement of the crystal structure of skutterudite, $CoAs_3$. *Acta Cryst.* B27, 2288-2289.

McCLURE, V. E. (1970): *Localized and Equivalent Orbitals.* Ph.D. thesis, University of California, San Diego.

OFFNER, F. (1934): A redetermination of the parameter for hauerite, MnS_2. *Z. Krist.* 89, 182-184.

PAULING, L. (1960): *The Nature of the Chemical Bond* (3rd ed.). Cornell Univ. Press, Ithaca, N.Y.

——— (1970): Crystallography and chemical bonding of sulfide minerals. *Mineral. Soc. Amer. Spec. Pap.* 3, 125-131.

——— (1975a): Maximum-valence radii of transition metals. *Proc. Nat. Acad. Sci. USA* 72, 3799-3801.

——— (1975b): Valence-bond theory of compounds of transition metals. *Proc. Nat. Acad. Sci. USA* 72, 4200-4202.

——— (1978a): Bond angles in transition-metal tricarbonyl compounds: A test of the theory of hybrid bond orbitals. *Proc. Nat. Acad. Sci. USA* 75, 12-15.

——— (1978b): Bond angles in transition-metal tetracarbonyl compounds: A further test of the theory of hybrid bond orbitals. *Proc. Nat. Acad. Sci. USA* 75, 569-572.

——— (1978c): The nature of the bonds formed by the transition metals with hydrogen, carbon, and phosphorus. *Acta Cryst.* B34, 746-752.

——— & HUGGINS, M. L. (1934): Covalent radii of atoms and interatomic distances in crystals containing electron-pair bonds. *Z. Krist.* 87, 205-238.

RAJAMANI, V. & PREWITT, C. T. (1974): The crystal structure of millerite. *Can. Mineral.* 12, 253-257.

SMITHELLS, C. J. (1949): *Metals Reference Book.* Interscience, New York.

STEVENS, E. C. & COPPENS, P. (1978): High resolution experimental electron density distribution of pyrite. *Amer. Cryst. Assoc. Meet., Norman, Oklahoma* (Abstr.).

SUTARNO, KNOP, O. & REID, K. I. G. (1967): Chalcogenides of the transition elements. V. Crystal structures of the disulfides and ditellurides of ruthenium and osmium. *Can. J. Chem.* 45, 1391-1400.

Received March 1978, revised manuscript accepted June 1978.