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The Crystal and Molecular Structure of Neutral Bis(ethylene-1,2-dithiolene) Complexes of Palladium and Platinum. Evidence for Metal–Metal Bonding

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The structures of two neutral bis(ethylene-1,2-dithiolene) complexes, $MS_4C_4H_4$, where M = Pd or Pt, have been determined by single-crystal X-ray diffraction using complete three-dimensional data obtained on a GE 490 automated diffractometer. The compounds are isostructural and crystallize in the monoclinic space group $P2_1/n$ with $Z = 4$; for $PdS_4C_4H_4$, $a = 9.916$ (3) Å, $b = 11.788$ (4) Å, $c = 6.472$ (3) Å, $\beta = 92.21$ (2)°; for $PtS_4C_4H_4$, $a = 9.973$ (5) Å, $b = 11.868$ (8) Å, $c = 6.477$ (6) Å, $\beta = 92.12$ (5)°. The structure was solved by Patterson and Fourier methods and refined by least squares to a final R factor of 0.059 (1349 reflections) for $PdS_4C_4H_4$ and 0.081 (1116 reflections) for $PtS_4C_4H_4$. The molecular units in each case have an approximately square-planar arrangement of S about the metal, with two $MS_4C_4H_4$ units in eclipsed relationship joined by Pd–Pd and Pt–Pt bonds of 2.790 (2) and 2.748 (2) Å, respectively, to form a dimeric structure. These dimers have a distorted cubic arrangement of S atoms with metal atoms pulled in toward each other from the centers of two opposite faces. They represent the first examples of dimeric metal–metal bonded 1,2-dithiolene complexes. Bond distances and angles within the chelate rings are similar to those observed for other neutral 1,2-dithiolene complexes.

Introduction

The crystal and molecular structures of 1,2-dithiolene complexes, well known for their reversible redox behavior and extensive ground-state π-electron delocalization, have received considerable attention recently.[1,2] Of particular interest have been the bis complexes of the type $[MS_4C_4R_4]^{0,1-,2-}$ (R = CH_3, CF_3, CN, C_6H_5, etc., and M = many of the transition metals) which have been found to exhibit a square-planar configuration for a wide variety of metals, substituents, and overall oxidation states.

The bulk of these complexes are monomeric, although a tendency toward pairwise association in the solid state, through metal–sulfur interactions, has been noted in some cases.[3] Discrete dimeric units, on the other hand, have been identified both in the solid and in solution for certain complexes where M = Co and Fe;[4] in all of these cases, interactions between $MS_4C_4R_4$ units are of the metal–sulfur type with no direct metal–metal bonding. We now report the first examples of dimeric bis(1,2-dithiolene) complexes in which metal–metal bonding plays an important role in the formation of the dimer units. These complexes are derivatives of the unsubstituted ethylene-1,2-dithiolate ligand $(S_2C_2H_2)^{2-}$ and have the empirical formula $MS_4C_4H_4$, where M = Pd and Pt.

In the course of investigating the physical properties of complexes of this ligand, a sharp contrast between $NiS_4C_4H_4$ and $MS_4C_4H_4$ (M = Pd, Pt) was observed both in solid-state electrical conductivity behavior and in the nature of the X-ray powder diffraction patterns. Accordingly, we undertook a single-crystal structure study with X-rays for each of the three complexes. Preliminary details of the $NiS_4C_4H_4$ structure were reported by Höhne, *et al.*, in 1966[5] and by Smith in 1967.[6] Smith has recently completed a thorough structural investigation of $NiS_4C_4H_4$, to be published in the near future.[7] Our findings confirm Smith's results in all essential details; therefore, only that information on $NiS_4C_4H_4$ which is relevant to the discussion of its Pd and Pt analogs shall be presented here.

In an earlier communication, we reported the preparation of two new examples of bis(ethylene-1,2-dithiolene) complexes, the neutral Pd and Pt derivatives, along with a preliminary account of their molecular structure.[8] In this paper we present the completed structure solution for these two complexes. We believe this to be the first example of a three-dimensional crystal structure determination for any bis(1,2-dithiolene) complex of Pd or Pt.

Experimental Section

(1) **Preparation and Analysis.**—The anionic complexes $[MS_4C_4H_4]^-$, with M = Ni, Pd, or Pt, were prepared by the method of Hoyer, *et al.*,[9] in the form of the Pr_4N^+ salt. Precipitation of the neutral complexes readily occurred upon I_2 oxidation of the corresponding salts in CH_3CN solution. Single crystals were grown from saturated CS_2 solutions by slow cooling and evaporation. The solubility of the complexes in CS_2 was in the order Ni > Pt ≫ Pd, so that only very small amounts of $PdS_4C_4H_4$ could be purified; consequently no elemental analysis was performed for $PdS_4C_4H_4$. *Anal.* Calcd for $PtS_4C_4H_4$: C, 12.8; H, 1.07; S, 34.2. Found: C, 13.0; H, 1.1; S, 34.3.

(2) **Molecular Weight and Mass Spectral Data.**—Molecular weight and mass spectral measurements were performed by the Materials Characterization Operation of General Electric Corporate Research and Development. Molecular weights were obtained using a Mechrolab vapor pressure osmometer with hexachlorobenzene and triphenylmethane as standards. The experimental molecular weight of $NiS_4C_4H_4$ (FW 239.04) was 247 in benzene (7×10^{-3} M) and 242 in chloroform (5×10^{-3} M); for $PtS_4C_4H_4$ (FW 375.42), the experimental molecular weights were 407 (average of two determinations) in benzene (2×10^{-3} M) and 376 in chloroform (1.5×10^{-3} M). In the case of $PtS_4C_4H_4$, measurements were made near the upper limit of concentration; $PdS_4C_4H_4$ was too insoluble for molecular weight determinations.

Mass spectral data were obtained at 120° for $PtS_4C_4H_4$ using a CEC21-104 mass spectrometer and show an intense peak at m/e 375 corresponding to the parent ion, ${}^{195}Pt{}^{32}S_4{}^{12}C_4H_4{}^+$, along with two peaks nearly as intense at m/e 374 and 376 for the corre-

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[1] J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).

[2] R. E. Eisenberg, *ibid.*, **12**, 295 (1970).

[3] J. H. Enemark and J. A. Ibers, *Inorg. Chem.*, **7**, 2636 (1968).

[4] W. C. Hamilton and I. Bernal, *ibid.*, **6**, 2003 (1967); J. H. Enemark and W. N. Lipscomb, *ibid.*, **4**, 1729 (1965); M. J. Baker-Hawkes, Z. Dori, R. Eisenberg, and H. B. Gray, *J. Amer. Chem. Soc.*, **90**, 4253 (1968).

[5] E. Höhne, P. Prokop, and E. Hoyer, *Z. Chem.*, **6**, 71 (1966).

[6] A. E. Smith, Abstracts, American Crystallographic Association Meeting, Minneapolis, Minn., Aug 1967.

[7] A. E. Smith, personal communication, Shell Development Corp., Emeryville, Calif.

[8] K. W. Browall, L. V. Interrante, and J. S. Kasper, *J. Amer. Chem. Soc.*, **93**, 6289 (1971).

[9] E. Hoyer, W. Dietzsch, H. Hennig, and W. Schroth, *Chem. Ber.*, **102**, 603 (1969).

TABLE I
CRYSTAL DATA[a]

	$PdS_4C_4H_4$	$PtS_4C_4H_4$
a, Å	9.916 (3)	9.973 (5)
b, Å	11.788 (4)	11.868 (8)
c, Å	6.472 (3)	6.477 (6)
β, deg	92.21 (2)	92.12 (5)
Z	4	4
Space group	$P2_1/n$	$P2_1/n$
D_X, g/cm³	2.490	3.255
D_M, g/cm³		>3.0
Linear abs coeff, μ, cm^{-1}	291.5	439
Crystal color	Black	Black
Crystal shape	Cross section bounded by (110) and ($\bar{1}$10); other faces somewhat irregular	Needles; needle axis [001], rectangular cross section bounded by (110) and ($\bar{1}$10)
Dimensions, cm	0.0052 × 0.0092 0.0110	0.0037 × 0.00463 × 0.0324
μr(max)	1.750	7.11
μr(min)	0.758	0.812

[a] Absorption corrections were made with program HORSE: W. C. Hamilton, unpublished work, Brookhaven National Laboratory, Upton, N. Y.

sponding ions with ^{194}Pt and ^{196}Pt, respectively. No peaks were observed near an m/e corresponding to a dimer.

(3) **Crystal Data.**—Preliminary studies with the precession technique, using Mo Kα X-rays, established the space group to be $P2_1/n$ for each compound. Complete three-dimensional single-crystal X-ray diffraction data were taken with Ni-filtered Cu Kα radiation with the GE 490 computer-controlled automated diffractometer. Accurate lattice parameters were obtained from measurements made manually with the diffractometer for approximately 20 reflections. These parameters and other crystal data are summarized in Table I.

(4) **Data Collection and Reduction.**—Procedures were the same for each crystal except when noted.

Goniometer	Diffractometer, GE 490, four circle, computer controlled
Spindle axis	a^*–c^*
Geometry	Takeoff angle of 4°
Detector	Scintillation counter with pulse height discrimination.
Radiation	Ni filtered, Cu Kα, λ 1.5418 Å
Maximum 2θ	150°
Intensities	θ–2θ step scan. Step = 0.05° in 2θ. Counting time 0.5 sec per step. Scan length = $3(1 + 0.25 \tan\theta)$, centered on θ. Background counts at each end of scan for half-time taken for scan.
Intensity standards	Three different reflections monitored every 50 reflections
Independent reflections observed	1560 for $PdS_4C_4H_4$; 1504 for $PtS_4C_4H_4$
Rejection scheme	$I < 2\sigma(I)$ for $PdS_4C_4H_4$; $I < 3\sigma(I)$ for $PtS_4C_4H_4$
Weights	$\sigma(F) = (1/2F)[\sigma_c^2 + (0.05F^2)^2]^{1/2}$, where σ_c^2 = counting variance; $w(F) = 1/\sigma^2(F)$
Independent reflections used	1349 for $PdS_4C_4H_4$; 1116 for $PtS_4C_4H_4$
Data processing	All raw data were corrected for background and drift in intensities of standards. Lorentz–polarization factors were applied

Programs used were the following

CONVAG	Converts magnetic tape output (in ASC-II code) into GE 600 system-standard format (L. Vogt[10])
PONCH, CARD-TO-TAPE, DATRDN, SORT, DASORT	Routines for processing, editing, and sorting raw data, including corrections for drift in standards and Lorentz–polarization factors and determination of standard deviations on basis of counting statistics (L. Vogt[10])
HORSE	Absorption corrections for polyhedral crystals (W. C. Hamilton[11])
BNLSI	Busing, Martin, and Levy[12] least-squares program modified by Brookhaven National Laboratory
FORDAP	Zalkin[13] Fourier program modified by Brookhaven National Laboratory
ORFFE	Bond distances, angles, and least-squares planes (Busing–Martin–Levy[14]) modified by Brookhaven National Laboratory
ORTEP	Plotting program (C. K. Johnson[15])
LIST	Listing of F's suitable for publication (W. C. Hamilton and R. Snyder[16])

Solution and Refinement of the Structures

Single crystals of $PdS_4C_4H_4$ were not available at the outset of our investigation; therefore the structure study of $PtS_4C_4H_4$ was undertaken first, despite the greater difficulties to be expected in coping with the especially heavy scattering and absorption of Pt. The positional coordinates for the Pt and S atoms in the asymmetric unit were obtained readily from the three-dimensional Patterson function and it was apparent that short Pt–Pt distances (~2.8 Å) and a dimeric unit were characteristic of the structure. Following refinement by least squares (three cycles) of the Pt and S parameters, Fourier and difference Fourier maps revealed the positions of the four carbon atoms of the asymmetric unit. Further refinement by least squares with the nine atoms resulted in a value of 0.081 for R (where $R = [\Sigma||F_o| - |F_c||/\Sigma|F_o|]$) and a value of 0.099 for the weighted R (where $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$). Anisotropic thermal parameters were determined for Pt and S, and the isotropic B parameter was evaluated for carbon; a correction for anomalous dispersion was made for Pt ($\Delta f' = -5.0$, $\Delta f'' = 8.0$). While the overall structure exclusive of hydrogen atoms was well established, the standard deviations of positional parameters and of bond lengths were somewhat high, except for Pt parameters and the Pt–Pt distance (see Tables IV and VI). Also, Fourier and difference Fourier maps contained maxima, in improbable locations, that approached those of carbon atoms. At this time, single crystals of $PdS_4C_4H_4$ became available. It seemed that greater precision could be achieved for the Pd compound, not only because of the presence of a lighter metal atom but also because of a more favorable morphology for these crystals.

The procedure for structure solution and refinement of $PdS_4C_4H_4$ was similar to that described for $PtS_4C_4H_4$. Again, Pd and S positions were given by the Patterson function and carbon positions were revealed from a Fourier with phases determined by Pd and S. The background in the electron density maps was much lower than for the Pt compound and even likely hydrogen positions were indicated. The ultimate least-squares refinement included all 13 atoms in the asymmetric unit with anisotropic thermal parameters for all atoms except hydrogen and a correction for anomalous scattering by Pd and S (for Pd, $\Delta f' = -0.5$, $\Delta f'' = 4.3$; for S, $\Delta f' = 0.3$, $\Delta f'' = 0.6$). The R value was 0.059 and the weighted R was 0.075 (as defined above). Hydrogen atom positions cannot be claimed with any great certainty, and their exclusion from the least-squares treatment hardly affects the R value; the deviations on their positions are large when they are included and spurious peaks occur in the electron density map of the same magnitude as those associated with hydrogen atoms. The situation regarding the other atoms in $PdS_4C_4H_4$, however, is much more satisfactory than for $PtS_4C_4H_4$, regarding precision in the determined parameters. It is clear, nonetheless, that, apart from the M–M distance, corresponding

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[10] L. Vogt, Report No. 69-C-273, General Electric Co., Research and Development Center, Schenectady, N. Y., 1969.

[11] W. C. Hamilton, unpublished work, Brookhaven National Laboratory, Upton, N. Y.

[12] W. R. Busing, K. O. Martin, and H. A. Levy, ORFLS, a Fortran crystallographic least-squares program, Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

[13] A. Zalkin, unpublished work, Lawrence Berkeley Laboratory, Berkeley, Calif.

[14] W. R. Busing, K. O. Martin, and H. A. Levy, ORFFE, a Fortran crystallographic function and error program, Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

[15] C. K. Johnson, ORTEP, a Fortran thermal ellipsoid plot program for crystal structure illustrations, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

[16] W. C. Hamilton and R. Snyder, unpublished work, Brookhaven National Laboratory, Upton, N. Y.

distances and angles in the two compounds are not significantly different (see Table VI).

The final lists of calculated and observed structure factors for both structures are given in Tables II and III.[17] The atomic scattering factors for Pd and Pt used in F_c were those of Cromer and Waber[18a] and the scattering factors for S, C, and H were the neutral atom values given in ref 18b. The anomalous dispersion corrections also were taken from ref 18b.

TABLE IV

POSITIONAL PARAMETERS

	x	*y*	*z*
		$PdS_4C_4H_4$	
Pd	0.09219 (6)	0.08417 (6)	0.06053 (1)
S(1)	−0.0726 (3)	0.1900 (2)	0.2150 (4)
S(2)	−0.2740 (2)	0.0051 (2)	0.0820 (4)
S(3)	−0.1459 (3)	0.0079 (2)	−0.3657 (4)
S(4)	0.0530 (3)	0.1882 (2)	−0.2364 (4)
C(1)	−0.1247 (10)	0.2786 (9)	0.0214 (20)
C(2)	−0.3393 (10)	0.0827 (10)	−0.1192 (19)
C(3)	−0.2815 (11)	0.0867 (9)	−0.3078 (19)
C(4)	−0.0664 (12)	0.2787 (9)	−0.1671 (20)
H(1)	−0.166 (18)	0.332 (15)	0.099 (27)
H(2)	−0.399 (14)	0.125 (12)	−0.071 (22)
H(3)	−0.327 (10)	0.142 (9)	−0.412 (16)
H(4)	−0.117 (16)	0.321 (13)	−0.280 (25)
		$PtS_4C_4H_4$	
Pt	0.09043 (9)	0.08220 (9)	0.05967 (18)
S(1)	−0.0699 (6)	0.1896 (6)	0.2154 (12)
S(2)	−0.2722 (6)	0.0042 (7)	0.0810 (12)
S(3)	−0.1467 (6)	0.0071 (6)	−0.3648 (11)
S(4)	0.0538 (7)	0.1875 (6)	−0.2323 (11)
C(1)	−0.1188 (27)	0.2785 (24)	0.0266 (49)
C(2)	−0.3384 (27)	0.0802 (25)	−0.1041 (47)
C(3)	−0.2859 (30)	0.0842 (29)	−0.3001 (53)
C(4)	−0.0671 (28)	0.2832 (24)	−0.1711 (50)

The positional and thermal parameters for both structures are listed in Tables IV and V. Table VI contains the principal interatomic distances and angles for both $PdS_4C_4H_4$ and $PtS_4C_4H_4$.

The labeling of atoms is according to the scheme shown in Figure 1.

Description of Structure

The molecular structure (Figures 1, 2) consists of two approximately planar $MS_4C_4H_4$ units joined by a direct metal–metal bond to form a $(MS_4C_4H_4)_2$ dimeric unit with an inversion center at the midpoint of the metal–metal bond. The orientation of the two $MS_4C_4H_4$ units is such that an approximate cube is outlined by the eight sulfur positions as indicated by the dashed lines in Figure 1. The most significant deviation of the actual structure from this idealized description is the lack of planarity of the $MS_4C_4H_4$ unit, which always is planar in the monomeric structures. The individual five-membered rings of a $MS_4C_4H_4$ unit, MS(1)C(1)C(4)S(4) and MS(2)′C(2)′C(3)′S(3)′, are much more nearly planar; however, they are not coplanar. They form angles of 171.8° (M = Pd) and 168.7° (M = Pt). The equations of the least-square planes for the five-membered rings are given in Table VII. Since one $MS_4C_4H_4$ unit may be taken as also the asymmetric unit of the structure, the two five-membered rings are not required to be equivalent, but they are indicated to be chemically equivalent within experimental error with respect to bond distances and angles.

The approximately cubic arrangement of sulfur atoms is more precisely that of an almost rectangular parallelepiped with three distinctly different edges. The shortest S–S distances are for edges parallel to the M–M bond, namely, for S(1)–S(2) and S(3)–S(4) with an average value of 3.03 ± 0.03 Å for M = Pd and 3.06 ± 0.03 Å for M = Pt. The next shortest edges correspond to the intraligand S–S separations, S(1)–S(4) and S(2)–S(3), with average values of 3.21 ± 0.01 and 3.19 ± 0.01 Å for Pd and Pt, respectively. The longest edges are formed by the interligand S–S distances within one $MS_4C_4H_4$ unit; their average values are 3.30 ± 0.01 Å (Pd) and 3.29 ± 0.02 Å (Pt). The deviation of the individual S–S distances (Table VI) from the average values just quoted is insignificant for the two longer edges, but this is not the case for the

TABLE V

THERMAL PARAMETERS[a]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
			$PdS_4C_4H_4$			
Pd	0.00492 (7)	0.00299 (5)	0.01591 (19)	−0.00002 (4)	−0.00060 (8)	0.00018 (7)
S(1)	0.0072 (3)	0.0043 (2)	0.0189 (6)	0.0009 (2)	0.0007 (3)	−0.0002 (3)
S(2)	0.0065 (2)	0.0052 (2)	0.0207 (7)	0.0010 (1)	0.0021 (3)	0.0007 (3)
S(3)	0.0071 (2)	0.0042 (2)	0.0174 (6)	0.0009 (2)	−0.0008 (3)	0.0007 (2)
S(4)	0.0069 (2)	0.0046 (2)	0.0193 (6)	0.0011 (2)	0.0012 (3)	0.0021 (3)
C(1)	0.0058 (9)	0.0040 (7)	0.0253 (31)	0.0010 (6)	−0.0003 (14)	−0.0005 (12)
C(2)	0.0048 (9)	0.0062 (8)	0.0230 (29)	0.0026 (7)	0.0010 (13)	0.0008 (13)
C(3)	0.0070 (10)	0.0048 (8)	0.0225 (29)	0.0004 (7)	−0.0009 (13)	0.0004 (12)
C(4)	0.0082 (11)	0.0038 (7)	0.0256 (32)	0.0021 (7)	0.0027 (15)	0.0036 (12)
			$PtS_4C_4H_4$			
Pt	0.00571 (10)	0.00437 (8)	0.01832 (32)	0.00004 (6)	0.00015 (12)	0.00040 (10)
S(1)	0.0074 (6)	0.0057 (5)	0.0178 (18)	−0.0007 (4)	−0.0018 (8)	−0.0017 (8)
S(2)	0.0069 (6)	0.0068 (5)	0.0204 (20)	−0.0005 (4)	−0.0028 (9)	−0.0002 (9)
S(3)	0.0079 (6)	0.0050 (4)	0.0155 (17)	−0.0007 (4)	0.0012 (8)	0.0003 (8)
S(4)	0.0081 (6)	0.0053 (6)	0.0167 (18)	−0.0004 (4)	−0.0003 (9)	0.0022 (8)
C(1)	3.4 (5)[b]					
C(2)	3.3 (5)[b]					
C(3)	4.1 (6)[b]					
C(4)	3.6 (5)[b]					

[a] Anistropic temperature factors are expressed as $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$; isotropic temperature factors are of the form $\exp(-B(\sin^2\theta)/\lambda^2)$. Standard deviations are in parentheses. [b] Isotropic B parameter.

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[17] Tables II and III, listings of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1800. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

[18] (a) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965): (b) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

Table VI

Principal Intramolecular Distances and Angles

	Distances, Å			Angles, deg	
	M = Pd	M = Pt		M = Pd	M = Pt
M–M	2.790 (2)	2.748 (2)	S(1)–M–S(3)′	91.6 (1)	91.7 (3)
M–S(1)	2.314 (3)	2.308 (7)	S(2)′–M–S(4)	91.1 (1)	91.1 (3)
M–S(2)′	2.310 (3)	2.302 (7)	S(1)–M–S(4)	88.5 (1)	88.2 (3)
M–S(3)′	2.298 (3)	2.293 (7)	S(2)′–M–S(3)′	88.3 (1)	88.0 (3)
M–S(4)	2.300 (3)	2.284 (7)	M–S(1)–C(1)	102.3 (4)	102.5 (11)
S(1)–C(1)	1.70 (1)	1.67 (3)	M–S(4)–C(4)	102.4 (4)	105.2 (11)
S(2)–C(2)	1.70 (1)	1.62 (3)	M–S(2)′–C(2)′	102.7 (4)	105.0 (11)
S(3)–C(3)	1.69 (1)	1.73 (3)	M–S(3)′–C(3)′	103.2 (4)	102.0 (12)
S(4)–C(4)	1.67 (1)	1.71 (3)	S(1)–C(1)–C(4)	122.1 (8)	125.9 (22)
C(1)–C(4)	1.37 (2)	1.40 (4)	S(2)–C(2)–C(3)	122.8 (8)	122.5 (23)
C(2)–C(3)	1.37 (2)	1.39 (4)	S(3)–C(3)–C(2)	122.9 (9)	122.5 (25)
C(1)–H(1)	0.91 (18)		S(4)–C(4)–C(1)	124.5 (9)	118.2 (23)
C(2)–H(2)	0.84 (14)				
C(3)–H(3)	1.03 (11)				
C(4)–H(4)	1.00 (16)				
Nonbonded Atoms					
⎰S(1)–S(2)	3.058 (4)	3.088 (10)	S(3)′–S(1)–S(2)	89.6 (1)	89.5 (3)
⎱S(3)–S(4)	2.997 (4)	3.030 (10)	S(3)′–S(1)–S(4)	89.5 (1)	89.5 (2)
⎰S(1)–S(4)	3.220 (4)	3.195 (10)	S(2)–S(1)–S(4)	90.6 (1)	90.5 (3)
⎱S(2)–S(3)	3.208 (4)	3.191 (11)	S(1)–S(2)–S(4)′	89.3 (1)	89.5 (3)
⎰S(1)–S(3)′	3.306 (4)	3.301 (10)	S(1)–S(2)–S(3)	88.3 (1)	88.4 (3)
⎱S(2)–S(4)′	3.290 (4)	3.274 (10)	S(4)′–S(2)–S(3)	90.0 (1)	89.9 (2)
			S(2)–S(3)–S(1)′	90.2 (1)	90.1 (3)
			S(2)–S(3)–S(4)	92.0 (1)	91.7 (2)
			S(1)′–S(3)–S(4)	90.1 (1)	90.0 (2)
			S(2)′–S(4)–S(1)	90.3 (1)	90.7 (3)
			S(2)′–S(4)–S(3)	91.0 (1)	91.0 (3)
			S(1)–S(4)–S(3)	89.1 (1)	89.4 (3)

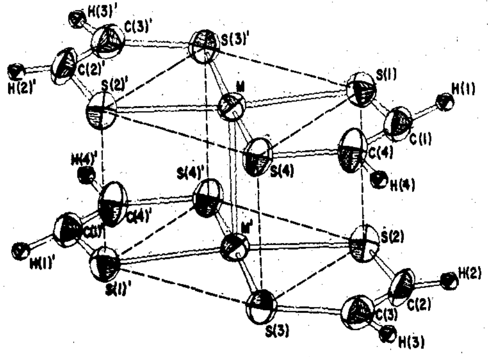

Figure 1.—Molecular structure of $[MS_4C_4H_4]_2$ showing orientation of thermal ellipsoids.

shortest distances S(1)–S(2) and S(3)–S(4). The respective values of 3.058 (4) and 2.997 (4) Å (M = Pd) appear significantly different. This inequality in the two short S–S distances and the significant deviation of several S–S–S angles from 90° cause a distortion of the dimeric unit from a more regular molecule with *mmm* symmetry. The true symmetry is only $\bar{1}$. While it is difficult to rule out the possibility that the small distortions are merely the consequence of systematic errors, they probably are real. The distances and angles for $PtS_4C_4H_4$, although with larger standard deviations, produce the same kind of distortions to the same degree. Furthermore, it is quite possible that the deviations from higher symmetry are the consequence of intermolecular interactions. The shortest intermolecular distances all involve S(3) and are shorter than the van der Waals distance of 3.70 Å. The intermolecular separations in $PdS_4C_4H_4$ are 3.438(6) Å for S(3)–S(3), 3.557(6) Å for S(3)–S(1), and 3.607 (6) Å for S(3)–S(4) with values slightly larger by 0.02–0.04 Å for $PtS_4C_4H_4$. By contrast, the shortest intermolecular S–S distance in $NiS_4C_4H_4$ is 3.737 (7) Å, essentially the van der Waals distance.

The packing of the dimeric units in the unit cell is shown in Figures 3 and 4. The staggered arrangement

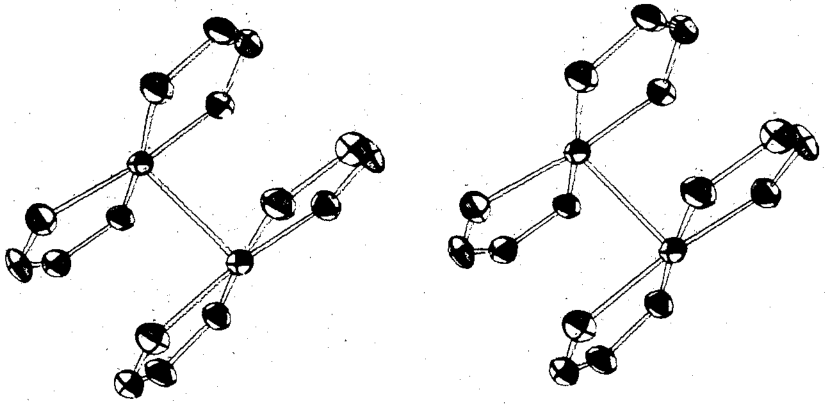

Figure 2.—Stereoscopic view of the $[MS_4C_4H_4]_2$ dimer.

TABLE VII

LEAST-SQUARES PLANES FOR M–S–C–C–S RINGS FROM EQUATIONS DEFINED BY $Ax + By + Cz = D$ (IN DIRECT CRYSTAL COORDINATE SYSTEM)

M	Plane	*A*	*B*	*C*	*D*
Pd	1	6.749	7.814	1.848	1.392
Pd	2	5.750	8.993	1.705	1.390
Pt	1	6.942	7.641	1.882	1.368
Pt	2	5.665	9.196	1.653	1.368

Atomic Displacements (Å) from Planes

M	Plane	
Pd	1	Pd (0.0000), S(1) (0.0002), C(1) (−0.0173), C(4) (0.0291), S(4) (−0.0005)
Pd	2	Pd (0.000), S(2)′ (−0.0001), C(2)′ (0.0201), C(3)′ (−0.0268), S(3)′ (0.0011)
Pt	1	Pt (0.000), S(1) (−0.001), C(1) (0.015), C(4) (−0.008), S(4) (−0.001)
Pt	2	Pt (0.000), S(2)′ (−0.003), C(2)′ (0.015), C(3)′ (0.026), S(3)′ (−0.002)

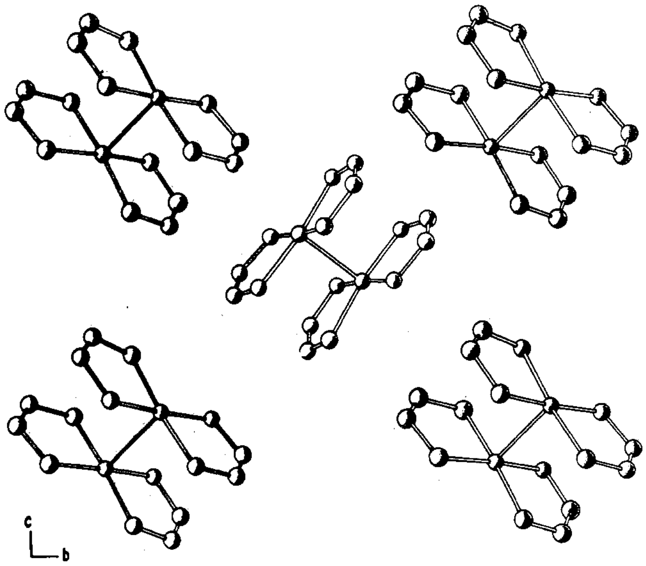

Figure 3.—Projection of the $[MS_4C_4H_4]_2$ structure on the *bc* plane.

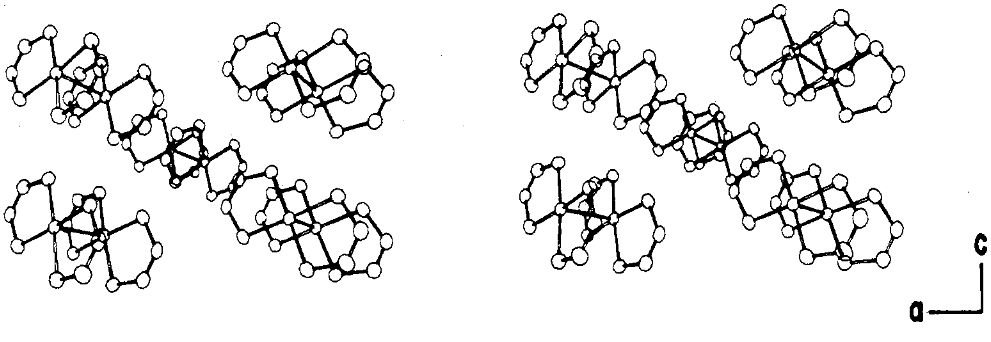

Figure 4.—Stereoscopic view down the *b* axis showing the packing of molecular units.

along the cell diagonal results in intermolecular contacts only between hydrogen atoms for units related by a body-diagonal translation. The closest nonhydrogen intermolecular contacts occur for units related by a translation in the *c* direction involving S(3), S(4), and S(1), as discussed in the previous paragraph.

The metal–metal distances (2.790 (2) Å for Pd–Pd and 2.748 (2) Å for Pt–Pt) are significantly shorter than the parallel S–S edges of the S_8 polyhedron and the metal atoms are drawn inward from two planes of sulfur atoms by 0.12 Å (Pd) and 0.16 Å (Pt). Thus the coordination geometry of the metal atoms is nearly tetragonal pyramidal with four essentially equal bonds to sulfur atoms and a bond to a metal atom in the fifth coordination position. The intraligand bond angles about the Pd atom are 88.5 (1) and 88.3 (1)° and less than the interligand angles of 91.6 (1) and 91.1 (1)°. Very nearly the same bond angle values are found for Pt.

Discussion

The molecular structures of $PdS_4C_4H_4$ and $PtS_4C_4H_4$ reported here represent an entirely new structural type for 1,2-dithiolene complexes. Particularly noteworthy are the occurrence of a metal–metal bond and the approximately cubic arrangement of the eight donor atoms. This is in contrast to the tendency for 1,2-dithiolenes to occur as discrete monomers with square-planar configuration. In some cases, such as $[(C_6H_5)_3ClP][Au(S_4C_4(CF_3)_4]$,[3] a weak pairwise association of the monomer units in the solid state has been noted. In addition, several dimeric bis(1,2-dithiolene) complexes have been identified; however, all of these exhibit a lateral displacement of the dimer halves with a resultant five-coordinate arrangement of sulfur atoms about each metal atom.[2] A third type of structure is the trigonal-prismatic geometry found for tris(1,2-dithiolene) complexes of Re, Mo, and V.[2] No direct metal–metal bond has been found in any of these previously studied structures.

The metal–metal distances of 2.790 (2) and 2.748 (2) Å in the $[MS_4C_4H_4]_2$ complexes are essentially the same as those in the metallic state of the elements and are among the shortest which have been observed in Pd or Pt complexes. Considerably longer metal–metal distances (3.25 Å) in complexes such as $Pt(NH_3)_4PtCl_4$[19] and $M(dmg)_2$, where M = Pd or Pt,[20] are known to have substantial effects upon electronic structure, as evidenced by both spectral and electrical conductivity measurements. Also, substantial metal–metal bonding has been inferred for the acetate-bridged dimer $[(\pi\text{-}C_3H_5)Pd(O_2CCH_3)]_2$ (Pd–Pd = 2.94 Å), on the basis of a comparison with the analogous $[Cu(O_2CCH_3)_2(H_2O)]_2$ structure.[21] A somewhat shorter metal–metal distance (2.65 Å) in the S-bridged complex $Pt_2S(CO)(P(C_6H_5)_3)_3$ has been considered to repre-

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[19] L. V. Interrante and F. P. Bundy, *Inorg. Chem.*, **10**, 1169 (1971).

[20] J. C. Zahner and H. G. Drickamer, *J. Chem. Phys.*, **33**, 1625 (1960).

[21] M. R. Churchill and R. Mason, *Nature (London)*, **204**, 777 (1964).

sent a single covalent platinum–platinum bond in agreement with the sum of the covalent radii (2.62 Å).[22] Recently, two additional examples of even shorter metal–metal bonds (2.58 Å) have been reported for palladium and platinum complexes with bridging organic π systems.[23]

The arrangement of the sulfur atoms in the $(MS_4C_4H_4)_2$ dimers is remarkable in several respects and suggests strongly that sulfur interactions are contributing appreciably to the stabilization of these structures. The unusual nearly cubic configuration of the S atoms with eclipsed ligand atoms is clearly not the one that would be chosen if minimization of interligand repulsive interactions were the important factor. Also, it is significant that the shortest S–S distances are those between $MS_4C_4H_4$ units and parallel to the M–M bond; these distances are considerably shorter than typical nonbonding S–S separations. The approximately square arrangement of sulfur atoms at the faces of the S_8 polyhedra and the short S–S distances do, however, bear some resemblance to the trigonal-prismatic geometry of the tris(1,2-dithiolene) complexes. Here, the six sulfur atoms form an approximately square-sided trigonal prism with interligand S–S separations of 3.07 Å close to the short distances of 3.058 (4) and 2.997 (4) Å between $PdS_4C_4H_4$ units. The suggestion that interdonor atom bonding may play an important role in stabilizing this highly unusual coordination geometry was made early in the work on such systems and has received considerable support from more recent structural studies. These studies have evidenced a close similarity between the dimensions of the trigonal prisms in the various tris(1,2-dithiolene) complexes that exhibit this structure with a near constancy of the interligand S–S distances.[2] Also, in an analogous tris(1,2-diselenene) complex where enhanced interdonor atom interactions might be anticipated on account of the larger size of the selenium valence orbitals, a similar trigonal-prismatic configuration with exceptionally short interligand Se–Se distances has been found.[24] The occurrence of this coordination geometry appears to be restricted to the neutral and some of the monoanionic tris(1,2-dithiolene) complexes where the oxidation state of the dithiolene ligands is closest to that of the 1,2-dithione formulation. In these complexes, the average C–S distance is 1.69 Å indicating considerable multiple-bond character in the C–S bonds and consequently a lower electron density on the S atoms.[2] In this context, it is noteworthy that the $MS_4C_4H_4$ (M = Ni, Pd, Pt) complexes also occur as the neutral species with C–S bond distances close to 1.69 Å.

The origin of the differences in the molecular structures of the three $MS_4C_4H_4$ complexes may be understood in terms of the effect of the metal atom upon the metal–metal and sulfur–sulfur interactions that are presumed to be important in stabilizing the eclipsed dimeric structure. In particular, the smaller valence orbitals of the Ni atom should lead to a much less effective metal–metal bonding at the internuclear distances encountered in the Pd and Pt structures and presumably dictated, in part, by interligand nonbonding interactions. Moreover, these same valence orbitals could also play a significant role in determining the extent of interdonor atom bonding by removing electron density from the sulfur atoms through pπ–dπ bonding. Again, the larger valence orbitals of Pd and Pt should be much more effective in this regard, thus facilitating dimer formation in these cases.

The explanation for the apparent lack of a precedent for this molecular structure among previous 1,2-dithiolene complexes undoubtedly requires consideration of both electronic and steric factors; however, it is interesting that the $MS_4C_4H_4$ complexes contain ligand substituents which offer the least possible steric resistance to the attainment of the eclipsed dimeric configuration and that in the other known $[MS_4C_4R_4]^0$ (M = Pd, Pt; R = CH_3, CF_3, C_6H_5) complexes, in particular, quite substantial repulsive interactions between substituents would be anticipated in such a configuration.

In spite of the distortion from planarity of the $MS_4C_4H_4$ unit in the formation of the dimer, the bonding within the chelate rings is substantially the same as in $NiS_4C_4H_4$ and a number of other neutral dithiolene complexes.[2] The corresponding average distances and angles are shown below.

	M = Pd	M = Pt	M = Ni
C–C, Å	1.37 (1)	1.39 (5)	1.358 (7)
S–C, Å	1.69 (1)	1.68 (3)	1.687 (5)
S–C–C, deg	123.1 (10)	122.3 (29)	120.2 (4)
M–S–C, deg	102.7 (5)	103.7 (13)	103.9 (2)

Also, there are no unusual features associated with the metal–sulfur bonding. A square-planar or rectangular arrangement of four sulfurs about the metal atom occurs in various sulfides of Pd and Pt, even for different oxidation states, and the characteristic M–S distance then is ~2.3 Å. The distance is 2.30 Å in PdS_2[25] (square-planar sulfur arrangement) and 2.312 Å in PtS[26] (rectangular sulfur configuration). In $PdS_4C_4H_4$ and $PtS_4C_4H_4$ the corresponding average M–S distances are 2.306 and 2.300 Å. These values are close to those obtained by addition of the single-bond radii of Pauling,[27] which give 2.32 Å for Pd–S and 2.33 Å for Pt–S.

Despite the foregoing evidence for a reasonably stable dimeric structure in the solid state, indications are that virtually complete dissociation occurs in solution. Molecular weight determinations for $PtS_4C_4H_4$ in chloroform solution near saturation ($\sim 10^{-3}$ *M*) give very good agreement with the monomeric formulation and in benzene give values only slightly higher than that expected for the monomer. The corresponding Pd complex was found to be insufficiently soluble in these solvents for molecular weight determination. Mass spectral data for $PtS_4C_4H_4$ at 120° also indicate a monomeric structure for this complex in the vapor. Preliminary infrared spectral studies indicate appreciable shifts in certain absorption bands upon dissolution of the $PtS_4C_4H_4$ and $PdS_4C_4H_4$ complexes in sol-

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[22] A. C. Skapski and P. G. H. Troughton, *Chem. Commun.*, 170 (1969).

[23] G. Allegra, A. Immirzi, and L. Porri, *J. Amer. Chem. Soc.*, **87**, 1394 (1965); K. K. Cheung, R. J. Cross, K. P. Forrest, R. Wardle, and M. Mercer, *Chem. Commun.*, 875 (1971).

[24] C. G. Pierpont and R. Eisenberg, *J. Chem. Soc. A*, 2285 (1971).

[25] F. Grønvold and E. Røst, *Acta Chem. Scand.*, **10**, 1620 (1956).

[26] F. Grønvold, H. Haraldsen, and A. Kjekshus, *ibid.*, **14**, 1879 (1960).

[27] L. Pauling, *J. Amer. Chem. Soc.*, **69**, 542 (1947).

vents such as benzene, chloroform, and CS_2; however, in the case of $NiS_4C_4H_4$ it is noteworthy that there were no significant changes in infrared spectra under these conditions.

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Contribution from the Department of Chemistry,
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The Crystal and Molecular Structures of the Cis and Trans Isomers of Bis(trichlorogermanyl)tetracarbonylruthenium

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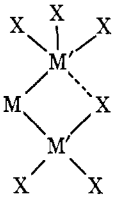
The crystal and molecular structures of the trans and cis isomers of bis(trichlorogermanyl)tetracarbonylruthenium have been determined. *trans*-$Ru(CO)_4(GeCl_3)_2$ crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions a = 9.152 (1) Å, b = 10.025 (1) Å, c = 8.399 (1) Å, β = 94.84 (1)°, and two molecules per unit cell (ρ_{obsd} = 2.46 g cm^{-3}, ρ_{calcd} = 2.47 g cm^{-3}). *cis*-$Ru(CO)_4(GeCl_3)_2$ crystallizes in monoclinic space group $P2_1$ with unit cell dimensions a = 9.759 (5) Å, b = 12.608 (10) Å, c = 12.878 (9) Å, β = 91.57 (10)°, and four molecules per unit cell (ρ_{obsd} = 2.40 (2) g cm^{-3}, ρ_{calcd} = 2.39 g cm^{-3}). Data were collected using counter methods and the structures were refined using least-squares procedures to give R = 0.019 and 0.041 for trans and cis isomers, respectively. Both structures contain discrete molecular species with octahedral coordination of the ruthenium atoms. The chemically different ruthenium–carbon distances in the cis isomer are not significantly different from each other—1.98 Å (trans to $GeCl_3$), 2.00 Å (trans to CO)—or from that observed in the trans isomer, 1.98 Å. The ruthenium–germanium distances are the same in both isomers (2.48 Å). These bond lengths are consistent with the force constant calculations that had suggested an unusual π-bonding ability for the trichlorogermanyl groups in these compounds.

Introduction

Compounds of the type $M(CO)_4(M'X_3)_2$ (where M = Fe, Ru, Os; M′ = Si, Ge, Sn; X = Cl, Br, I, alkyl, aryl) have been found to exist as cis and/or trans isomers.[1–6] There are several factors which can affect the relative stability of the cis and trans isomers. A consideration of π-bonding abilities for the ligands CO and $M'X_3$ suggests that any discrepancy (either CO $\gg$ $M'X_3$ or $M'X_3 \gg$ CO) would favor the cis isomers. These relative π-bonding abilities would be expected to vary with M, M′, and X. The other major factor influencing the preferred geometry involves intramolecular repulsions. Thus the investigations of Stone, *et al.*,[2,5] on trialkyl and triaryl, silyl, and stannyl derivatives of $Ru(CO)_4$, where definite equilibria were established, showed increasing preference for the trans structure as the bulkiness of the $M'R_3$ group increased. However, when X = a halogen in the cis compounds, an additional interaction may be possible but attractive in nature rather than repulsive. This is due to the potential to form intramolecular halogen bridges where the main group IV element increases its coordination number to 5. Thus Graham and Kummer[1] recognized the possible importance of structures I and II for *cis*-$M(M'X_3)_2$ fragments. While the formation of a weak halogen bridge has been demonstrated in bipy$(CO)_3$-$ClMoSnCH_3Cl_2$,[7] as yet there is no direct confirmation that cis $M'X_3$ groups do interact in this way.



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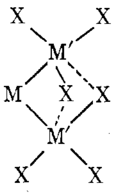

II

Of particular interest was the synthesis and isolation of both the cis and trans isomers of bis(trichlorogermanyl)tetracarbonylruthenium ($Ru(CO)_4(GeCl_3)_2$)[6] where the spectroscopic studies[8] suggested that the π-acceptor properties of $GeCl_3$ were comparable with those of carbon monoxide. The physical properties of the cis and trans isomers raised the question that the cis and trans isomers might contain intra- and intermolecular halogen to Ge bridge bonding, respectively.[6] The current structural study was undertaken to investigate these features.

Experimental Section

(a) *trans*-$\mathbf{Ru(CO)_4(GeCl_3)_2}$.—The white well-formed crystals, as supplied by Dr. W. A. G. Graham and Mr. R. K. Pomeroy, were found to be suitable for an X-ray diffraction study. The preliminary photography—$0kl$, $1kl$, $2kl$ (Cu Kα Weissenberg) and $h0l$, $hk0$ (Mo Kα precession)—showed the crystals to be monoclinic, and the systematic absences—$0k0$ for $k = 2n + 1$ and $h0l$ for $h + l = 2n + 1$—suggested the nonstandard space group $P2_1/n$. The lattice parameters and their estimated standard deviations were obtained at 22° as a = 9.152 (1) Å, b = 10.025 (1) Å, c = 8.399 (1) Å, and β = 94.84 (1)°, by a least-squares refinement using 2θ values for 12 high-angle reflections that had been accurately centered on a Picker manual four-circle diffractometer (Cu Kα_1 radiation, λ 1.54051 Å). The observed density, measured by flotation as 2.46 (2) g cm^{-3}, is in good agreement with that calculated, 2.47 cm^{-3}, for two mole-

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[1] R. Kummer and W. A. G. Graham, *Inorg. Chem.*, **7**, 1208 (1968).

[2] J. D. Cotton, S. A. R. Knox, and F. G. A. Stone, *J. Chem. Soc. A*, 2758 (1968).

[3] R. K. Pomeroy, M. Elder, D. Hall and W. A. G. Graham, *J. Chem. Soc. D*, 381 (1969).

[4] M. Pankowski and M. Bigorgne, *J. Organometal. Chem.*, **19**, 393 (1969).

[5] S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. A*, 2559 (1969).

[6] R. K. Pomeroy and W. A. G. Graham, in preparation.

[7] M. Elder and D. Hall, *J. Chem. Soc. A*, 245 (1970).

[8] R. Gray and W. A. G. Graham, in preparation.