Synthesis of Macrocyclic Mercury(II) Derivatives of *S,S'*-Trimethylene- and *S,S'*-Tetramethylenebis(*cis*-stilbene-α,β-dithiol) with Unusual Structures☆

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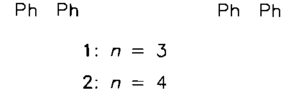
The reaction of the ligand *cis*-$^-$S–C(Ph)=C(Ph)–S–[CH$_2$]$_n$–S–C(Ph)=C(Ph)–S$^-$ with $n = 3$ (dianion of **1**) with HgCl$_2$ in ethanol produces a yellow linearly trinuclear, μ-S and μ-Cl-bridged complex of composition $C_{62}H_{52}Cl_2Hg_3S_8$ (**4**), in which the central Hg(II) ion is in a near octahedral arrangement of four Hg–S and two Hg–Cl bonds, whereas the two terminal Hg(II) ions are tetracoordinated with three Hg–S bonds and one Hg–Cl bond in distorted tetrahedral arrangements. The two ligands are bidentate with respect to the terminal and central Hg(II) ions. The corresponding ligand with $n = 4$ (dianion of **2**) reacts with HgCl$_2$ to yield a yellow Hg(II) complex of composition $C_{32}H_{28}HgS_4$ (**5**), in which the ligand is tetradentate and in the *trans-syn* configuration. The Hg(II) ion in the unit cell of **5** is pentacoordinated, due to symmetric dimerization of two molecules of **2** by two weak coordinate Hg–S bonds of 3.442(2) Å length.

In a recent paper[1] we showed that the unsaturated thiol thioethers **1**, **2** with $n = 3$ and 4 form remarkably stable, macrocyclic mononuclear Ni(II) derivatives.

In order to establish whether appropriately modified ligands of this type could be useful for heavy metal detoxification, especially of mercury, their coordination behavior with respect to Hg(II) was investigated. In the present paper, we report the structures of two complexes obtained on the reaction of **1** and **2** with HgCl$_2$ as determined in the solid state by single crystal X-ray methods and in solution by high-resolution ^{1}H-NMR measurements.

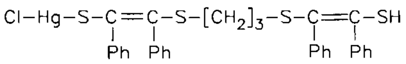


$$HS-\underset{Ph}{C}=\underset{Ph}{C}-S-[CH_2]_n-S-\underset{Ph}{C}=\underset{Ph}{C}-SH$$

1: $n = 3$
2: $n = 4$

Results and Discussion

On reaction of **1** with HgCl$_2$ in ethanol, only a chlorine-containing compound **4** of the composition $C_{62}H_{52}Cl_2Hg_3S_8$ was obtained, corresponding to a complex of the type $Hg_3L_4Cl_2$, where L is the dianion of **1**. The formation of **4** may be rationalized by assuming that **1** reacts with HgCl$_2$ initially to yield the chloromercaptide **3**, two molecules of which react with an additional molecule of HgCl$_2$ to yield **4**. Steric constraints are evidently no longer critical in the corresponding reaction of ligand **2** with HgCl$_2$, which under identical conditions produced a mononuclear mercaptide of composition $C_{32}H_{28}S_4Hg$ (**5**). Accordingly, ligands derived from **2** with hydrophilic substituents deserve for further studies on the selective sequestration and detoxification of mercury in biological systems.



$$Cl-Hg-S-\underset{Ph}{C}=\underset{Ph}{C}-S-[CH_2]_3-S-\underset{Ph}{C}=\underset{Ph}{C}-SH$$

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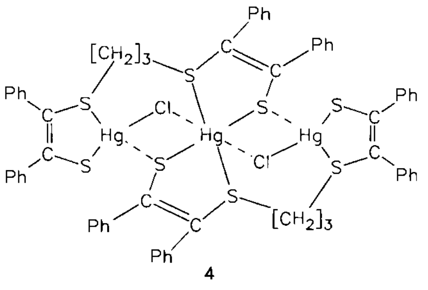

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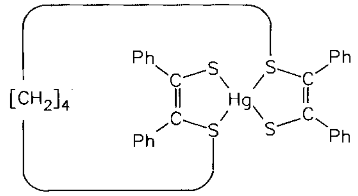

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Solid State Structures

Perspective drawings of the structures of both **4** and **5** as determined by single-crystal X-ray analysis are shown in

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Figures 1 and 2, positional parameters and their estimated standard deviations are given in Tables 1 and 2.

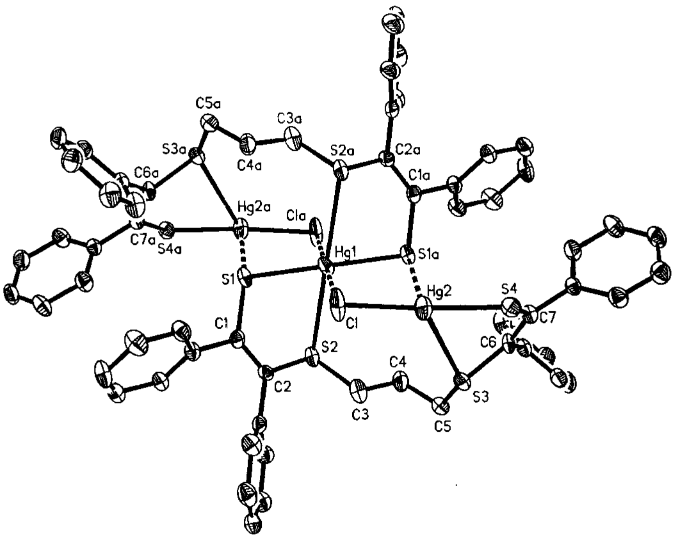

Figure 1. Perspective drawing of complex **4** with Hg, C, and S atoms numbered. The atoms are drawn with 30% probability ellipsoids

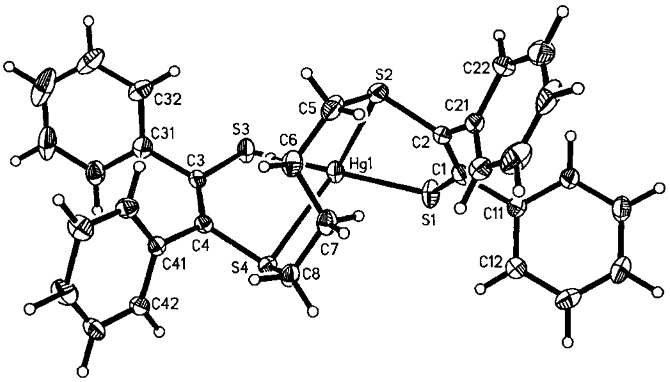

Figure 2. Perspective drawing of a monomeric unit of complex **5** with Hg, C, and S atoms numbered. The atoms are drawn with 30% probability ellipsoids

The three Hg ions in **4** are linked by two μ-S and two μ-Cl bonds; the $Hg_3\mu S_2\mu Cl_2$ unit is essentially planar. The central Hg atom Hg(1) is on a center of symmetry and is axially coordinated to the thioether sulfur atoms of different ligands. The in-plane Cl–Hg(1)–Cl and S–Hg(1)–S bond angles as well as the axial S–Hg(1)–S bond angle are 180°. The mean Cl–Hg(1)–S(1) and Cl–Hg(1)–S(2) bond angles are 90(3) and 90(8)°. The coordination geometry of Hg(1) may thus be viewed as distorted octahedral. The mean in-plane Hg(1)–S bonds of 2.381(2) Å are only slightly longer than the bonds to the nearest sulfur atoms in cinnabar (2.36 Å)[2] and similar to the shortest Hg–S bonds in the trinuclear anion[3] $[Hg_3(SCH_2CH_2S)_4]^{2-}$. The in-plane Hg(1)–Cl bonds have the lengths of 3.191(2) Å, indicating that these are coordinate Hg–Cl bonds. The Hg(2)–Cl bonds of 2.336(2) Å are significantly shorter than those involving the central mercury atom, essentially identical to those of $HgCl_2$ in the gas phase[4] and only slightly longer than those in solid $HgCl_2$[5], indicating that these are covalent rather than coordinate Hg–Cl bonds. In the complex $K_2HgCl_4 \cdot H_2O$ the Hg(II) ion also has two short and presumably covalent Hg–Cl bonds of 2.29 Å[6].

The in-plane bridging Hg–μS bonds from the peripheral Hg ions Hg(2) and Hg(2a) of 3.157(2) Å are slightly shorter than the Hg–μCl bonds, Hg(1)–Cl, of 3.191(2) Å. The peripheral coordinate Hg–S bond, Hg(2)–S(3), is 3.004(2) Å, and the two axial coordinate Hg–S bonds, Hg(1)–S(2) and Hg(1)–S(2a), are 2.981(2) Å.

In complex **5** the sulfur ligand is tetradentate as expected, but in contrast to a *cis-anti* configuration in the corresponding Ni(II) complex[1] an unexpected *trans-syn* configuration with respect to the $S[CH_2]_4S$ ligand moiety is realized. Moreover, **5** forms a centrosymmetric dimer in the solid state, with two weak coordinate Hg–S bonds of average length of 3.442(3) Å. The mercury atoms are in distorted pentacoordinated environments. The mean lengths of the covalent Hg–S bonds Hg(1)–S(1) and Hg(1)–S(3) of 2.356(2) and 2.368(2) Å are nearly equidistant and slightly longer than the covalent Hg–S bonds of 2.322(6) Å in a recently described[7] neutral substituted Hg thiophenolate of composition $Hg(S\text{-}2,4,6\text{-}i Pr_3C_6H_2)_2$. The bond angle S(1)–Hg(1)–S(3) in **5** of 165.4(1)° indicates a strong *trans*-directing influence; it is only slightly narrower than the corresponding angle in **1** [174.3(2)°]. The *trans*-directing influence of the Hg–S bonds is also responsible for the *trans-anti* configuration of the ligand $S\text{–}CH_2\text{–}$ residues. The two coordinate Hg–S bonds Hg(1)–S(2) and Hg(1)–S(4) have nearly the same length of 3.026(3) and 2.957(3) Å, respectively, and are within expected ranges and similar to the "short" coordinative HgS bonds in **4**. The corresponding angle S(2)–Hg(1)–S(4) is 108.2(1)°. The mean lengths of the thiolato and thioether C–S bonds of 1.76(1) and 1.77(1) Å are within expected ranges, as are those of the mean ethylenic C=C bonds of 1.345(11) Å and the associated bond angles. The angles Hg(1)–S(1)–C(1) and Hg(1)–S(3)–C(3) of 109.0(3) and 106.5(3)° are close to tetrahedral, but the angles involving coordinate Hg–S bonds show larger deviations from tetrahedral; Hg(1)–S(2)–C(2) being only 94.1(3)° and Hg(1)–S(2)–C(5), 106.0(3)°, for example, including bonds involving only carbon and sulfur, such as C(2)–S(2)–C(5), which is only 101.9(4)°. This is suggestive of some steric strain in the molecule. The two μS bonds linking the two mercury atoms, Hg(1)–S(4′) and Hg(1′)–S(4), of 3.442(3) Å are significantly longer than normal coordinate Hg–S bonds. The angles S(1)–Hg(1)–S(4′) and S(3)–Hg(1)–S(4′) are 79.0(1) and 91.2(1)°, respectively, indicating that the three sulfur atoms are arranged in a T-shaped fashion.

Structures in Solution

Variable-temperature ^1H-NMR studies of **4** and **5** in CD_2Cl_2 solution revealed no major changes in the temperature range $\pm 50\,°C$, suggesting the absence of dynamic ligand behavior in both compounds. This is attributed to the "locked-in" position of the ligands in both compounds, which may be viewed as a direct consequence of the high affinity of mercury for sulfur and its tendency to form three-dimensional sulfur-mercury networks.

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Experimental

All common laboratory chemicals were of reagent or analytical grade. Experiments were performed on a Schlenk-line under nitrogen where necessary. – Room-temperature and variable-temperature ^{1}H NMR: GE-300 instrument, 300 MHz. – The thiols **1** and **2** were prepared from the corresponding nickel complexes as described in Ref.[1]

Synthesis of Complex **4**: Ligand **1** (0.53 g, 1.0 mmol) was dissolved in 100 ml of hot ethanol and the solution added slowly to 10 ml of an aqueous solution of 0.27 g (1.0 mmol) of $HgCl_2$. Upon cooling, a light-yellow precipitate formed with was collected, dried, and recrystallized from CH_2Cl_2/acetone affording 0.45 g (0.26 mmol, 26%) of **4**, m.p. 141 °C. – ^{1}H NMR ($CDCl_3$): $\delta = 1.87$ (q, $J = 6.5$ Hz, 4H, CH_2), 2.72 (t, $J = 6.7$ Hz, 8H, SCH_2), 7.01–7.18 (m, 40H, Ph).

$C_{62}H_{52}Cl_2Hg_3S_8$ (1726.3)	Calcd.	C 43.14	H 3.04
	Found	C 43.36	H 3.18

Synthesis of Complex **5**: Ligand **2** (0.54 g, 1.0 mmol) was dissolved in 100 ml of hot ethanol and the solution added slowly to 10 ml of an aqueous solution of 0.27 g (1.0 mmol) of $HgCl_2$. Upon cooling a light-yellow precipitate formed which was collected, dried, and recrystallized from CH_2Cl_2/acetone affording 0.45 g (0.61 mmol, 61%) of **5**. m.p. 165 °C. – ^{1}H NMR ($CDCl_3$): $\delta = 1.83$ (br, s, 4H, CH_2), 2.60 (br s, 4H, SCH_2), 7.05–7.22 (m, 20H, Ph).

X-Ray Characterization of Complex **4**: A yellow prismatic crystal of **4** (approximate dimension 0.10 × 0.17 × 0.20 mm) was mounted on a glass fiber with its long axis roughly parallel to the phi-axis of the goniometer. Data collection was performed at 23 °C on an Enraf Nonius CAD4 computer-controlled kappa axis diffractometer equipped with a graphite crystal, incident beam monochromator and Mo-K_α radiation ($\lambda = 0.71073$ Å), using the $\Theta - 2\Theta$ scan technique. The scan rate varied from 1 to 5 deg/min (in ω). For weak reflections a slow scan rate was used. Data were determined as a function of Θ to correct for the separation of the K_α doublet; the scan width was calculated as $0.8 + 0.350 \tan\Theta$. Thus, the ratio of peak counting time to background counting time was 2:1. Cell constants and a orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 22 reflections in the range $11 < \Theta < 15°$ measured by the computer-controlled diagonal slit method of centering[8]. As a check on crystal quality, ω scans of several intense reflections were measured; the width and half-height was 0.40° with a take-off angle of 3.8° indicating moderate crystal quality. There were no systematic absences. For space $P\bar{1}$ (No. 2), the triclinic cell parameters and calculated volume are $a = 8.589(2)$, $b = 11.539(2)$, $c = 15.954(3)$ Å, $\alpha = 105.86(2)$, $\beta = 100.42(2)$, $\gamma = 95.72(2)°$, $V = 1477.2$ Å^3. For $Z = 1$ and formula weight 1726.29 the calculated density is 1.94 g/cm^3, $\mu = 81.8$ cm^{-1}. – A total of 4159 reflections were collected, of which 3610 were unique. The intensities of 3 representative reflections measured every 120 min remained constant within experimental error throughout data collection, hence no decay correction was necessary. Lorentz and polarization corrections were applied to the data. An empirical absorption correction based on scans was also applied, the relative range of transmission was 0.61–1.000, the relative transmission coefficients ranged from 0.610 to 0.998 with an average value of 0.834. The agreement factors for the averaging of the 1399 observed and accepted reflections was 1.6% based on F_o. The structure was solved using the Patterson heavy-atom method which revealed the positions of 2 atoms. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located or calculated and added to the structure factor calculations in idealized X-ray positions, but their positions were not refined. The structure was refined in full-matrix least-squares where the function minimized was $\Sigma w(|F_o| - |F|)^2$, and the weight w is defined as $4F^2/[(F^2)]^2$.

The standard deviation on intensities is defined as $(F^2) = (\sigma^2_{\text{counting}} + 0.050\ F^2)$. Scattering factors were taken from Cromer and Waber[9]. Anomalous dispersion effects were included in F_c[9]; the values for f' and f'' were those of Cromer[10]. Only the 3037 reflections with $F_c > 2.0\sigma(F_o^2)$ were used in the refinements. The final cycle of refinement included 340 variable parameters and converged (largest parameter shift was 0.05 times its esd) with unweighted and weighted agreement factors $R_1 = \Sigma\ |F_o| - |F_c|/\Sigma\ |F_o| = 0.033$, $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w\ |F_o|^2)^{1/2} = 0.045$. The standard deviation of an observation of unit weight was 1.35. The highest peak in the final difference Fourier had a height of 0.71 e/Å^3. All calculations were performed on a VAX computer using SDP/VAX[11,12].

X-Ray Characterization of **5**: The crystal structure of the complex **5** was solved on a Siemens R3m/V Diffractometer with Mo-K_α

Table 1. Positional parameters of **4** and their estimated standard deviations. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3) \cdot [a^2 \cdot \beta(1,1) + b^2 \cdot \beta(2,2) + c^2 \cdot \beta(3,3) + ab(\cos\gamma) \cdot \beta(1,2) + ac(\cos\beta) \cdot \beta(1,3) + bc(\cos\alpha) \cdot \beta(2,3)]$

Atom	x	y	z	B(Å^2)
Hg1	0.000	0.500	0.500	3.557(9)
Hg2	0.06828(4)	0.15535(3)	0.48018(2)	4.224(8)
C1	0.1896(4)	0.3310(2)	0.5963(2)	6.14(6)
S1	0.0754(2)	0.6742(2)	0.6284(1)	3.50(4)
S2	-0.2783(2)	0.5046(2)	0.5880(1)	3.44(4)
S3	-0.2841(2)	0.0706(2)	0.4546(1)	3.28(4)
S4	0.0014(2)	-0.0359(2)	0.3708(1)	3.64(4)
C1	-0.0105(8)	0.6296(6)	0.7098(5)	2.9(2)
C2	-0.1518(8)	0.5556(6)	0.6953(4)	2.7(2)
C3	-0.327(1)	0.3414(7)	0.5751(6)	4.6(2)
C4	-0.432(1)	0.2785(7)	0.4860(6)	4.3(2)
C5	-0.4593(9)	0.1448(7)	0.4720(5)	3.7(2)
C6	-0.3089(8)	0.0111(6)	0.3377(5)	2.8(2)
C7	-0.1893(8)	-0.0365(6)	0.3051(5)	3.0(2)
C8	0.0912(8)	0.6861(6)	0.8012(5)	2.8(2)
C9	0.0299(9)	0.7532(7)	0.8697(5)	3.5(2)
C10	0.128(1)	0.8067(8)	0.9551(5)	4.2(2)
C11	0.285(1)	0.7929(8)	0.9712(5)	4.6(2)
C12	0.347(1)	0.7243(9)	0.9028(6)	5.0(2)
C13	0.2507(9)	0.6721(7)	0.8178(5)	3.8(2)
C14	-0.2117(8)	0.5145(6)	0.7658(5)	3.0(2)
C15	-0.3701(9)	0.5164(7)	0.7735(5)	3.9(2)
C16	-0.430(1)	0.4740(8)	0.8356(6)	5.0(2)
C17	-0.334(1)	0.4238(7)	0.8908(6)	5.1(2)
C18	-0.174(1)	0.4215(7)	0.8839(6)	4.7(2)
C19	-0.115(1)	0.4640(7)	0.8219(5)	4.0(2)
C20	-0.4682(8)	0.0091(6)	0.2820(5)	3.0(2)
C21	-0.499(1)	0.1100(7)	0.2545(6)	4.4(2)
C22	-0.649(1)	0.1142(8)	0.2073(6)	5.1(2)
C23	-0.768(1)	0.0183(8)	0.1872(6)	5.2(2)
C24	-0.741(1)	-0.0839(8)	0.2115(6)	5.0(2)
C25	-0.5891(9)	-0.0899(7)	0.2585(5)	3.9(2)
C26	-0.2058(8)	-0.1039(6)	0.2103(5)	2.8(2)
C27	-0.231(1)	-0.0490(7)	0.1425(5)	4.1(2)
C28	-0.247(1)	-0.1167(8)	0.0539(5)	4.7(2)
C29	-0.241(1)	-0.2383(8)	0.0327(5)	4.4(2)
C30	-0.218(1)	-0.2952(8)	0.0980(6)	4.7(2)
C31	-0.199(1)	-0.2283(7)	0.1859(5)	4.1(2)

radiation ($\lambda = 0.71073$ Å) at 296 K using a highly oriented graphite crystal as a monochromator. With the 2Θ range from 4° to 50°, the $\Theta - 2\Theta$ scan mode was employed, the scan speed was variable, ranging from 2.50 to 5.00°/min in Θ. The scan range was 0.60°, plus K_α separation. Background measurement was performed using the stationary crystal and stationary counter at the beginning and end of each scan, each for 25% of total scan time; 3 standard reflections were measured every 200 reflections. Size of crystal used for analysis (mm): 0.28 × 0.36 × 0.44. Index ranges were $0 < h < 10$, $14 < k < 14$, $16 < l < 17$. A total of 5118 reflections were collected, of which 5088 were independent, there were 4382 observed reflections $F > 6.0(F)$. Absorption corrections were applied with a transmission range of 0.1946/0.2528. No systematic absences were observed. Space group $P\bar{1}$ (No. 2, C_i^1); until cell dimensions: $a = 8.622(4)$, $b = 12.12(5)$, $c = 14.749(7)$ Å, $\alpha = 73.74(4)$, $\beta = 76.99(4)$, $\gamma = 85.63(3)°$, $V = 1441.5(11)$ Å^3, $Z = 2$, formula weight 741.4, density calcd. 1.708 g/cm^3, absorption coefficient 5.636 mm^{-1}, $F(000)$, 728. – The structure of **5** was solved by Patterson methods using the full-matrix least-squares method and minimizing $w(F_o - F_c)^2$ with hydrogen atom positions assumed to fit the riding model, at fixed anisotropic U. The weighting scheme employed was $w^{-1} = \sigma^2(F) + 0.004F^2$. The final R was 3.92%, $wR = 5.68\%$ for observed data, for all data $R = 4.89\%$ and $wR = 7.22\%$, respectively. The goodness of fit was 2.08 and the data-to-parameter ratio was 13.1:1. The number of parameters was 334 and the largest difference peak and hole were 1.76 and -1.41 eÅ^{-3}, respectively.

Table 2. Atomic coordinates ($\cdot 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \cdot 10^3$) of complex **5**. Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor, i.e., $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \bar{a}_i \cdot \bar{a}_j$

	x	y	z	U(eq)
Hg(1)	5149(1)	3950(1)	3697(1)	38(1)
S(1)	6864(3)	2488(2)	4356(2)	50(1)
S(2)	7311(3)	3513(2)	1905(2)	44(1)
S(3)	2927(2)	5139(2)	3354(2)	46(1)
S(4)	6006(2)	6180(2)	3884(1)	35(1)
C(1)	8602(9)	2458(6)	3476(6)	37(3)
C(2)	8838(9)	2867(6)	2512(6)	35(3)
C(3)	3632(9)	6568(6)	2896(6)	34(3)
C(4)	4902(8)	7019(6)	3050(5)	28(2)
C(5)	8174(11)	4900(8)	1190(6)	51(3)
C(6)	7828(10)	5828(7)	1720(6)	45(3)
C(7)	8620(9)	5618(7)	2572(6)	42(3)
C(8)	8049(9)	6415(7)	3218(7)	44(3)
C(11)	9943(10)	1887(7)	3932(6)	38(3)
C(12)	10506(11)	2357(8)	4548(7)	51(4)
C(13)	11809(12)	1864(9)	4916(8)	62(4)
C(14)	12532(12)	919(9)	4695(8)	60(4)
C(15)	11947(11)	419(8)	4117(7)	52(4)
C(16)	10679(10)	908(7)	3724(6)	42(3)
C(21)	10427(9)	2821(7)	1869(5)	36(3)
C(22)	10682(11)	2113(7)	1232(6)	44(3)
C(23)	12175(13)	1996(10)	678(7)	62(4)
C(24)	13408(12)	2584(12)	718(7)	75(5)
C(25)	13199(11)	3341(11)	1312(8)	67(5)
C(26)	11725(10)	3431(8)	1885(6)	47(3)
C(31)	2576(9)	7285(7)	2265(6)	37(3)
C(32)	2498(10)	7035(8)	1411(6)	47(3)
C(33)	1544(13)	7695(10)	831(7)	66(4)
C(34)	647(15)	8593(11)	1072(11)	96(7)
C(35)	698(12)	8815(9)	1939(10)	71(5)
C(36)	1641(10)	8172(7)	2534(7)	49(3)
C(41)	5387(8)	8222(6)	2600(5)	30(2)
C(42)	5664(9)	8928(6)	3149(6)	36(3)
C(43)	6139(11)	10053(7)	2724(7)	49(4)
C(44)	6341(11)	10476(8)	1776(7)	55(4)
C(45)	6121(10)	9806(7)	1165(6)	47(3)
C(46)	5656(9)	8701(7)	1595(6)	39(3)

Supplementary Material Available: Tables of positional parameters, torsion angles and tables of least-square planes, a listing of observed and calculated structure factors and additional perspective drawings of the structures of complexes **4** and **5** may be obtained from G.N.S. The complete X-ray crystallographic data are deposited with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, FRG, and may be requested by quoting the depository number CSD-57033, the names of the authors and the full literature citation.

☆ Dedicated to Professor *Klaus Hafner* on the occasion of his 65th birthday.

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