

that determined for $(Cp_2Fe^+)(BiCl_4^-)^7$ (average $\approx 2.076 \text{ \AA}$)²⁶ appear to be marginally longer than that reported for ferrocene (2.058 \AA from electron diffraction^{24b} or 2.045 \AA from X-ray diffraction)²⁷ and for most ferrocene derivatives.²³

(3) The Fe-ring distances of 1.6987 (8) and 1.7045 (8) \AA (average = 1.7016 \AA) in the present structure agree with those determined in ordered ferrocenium structures—viz, 1.70 \AA in $(Cp_2Fe^+)(BiCl_4^-)^{7b}$ and 1.69 and 1.70 \AA in $[(\eta^5-C_5H_4Me)_2Fe^+](I_3^-)^{22}$. These values are, again, slightly larger than those found in ferrocene (1.66 \AA).²⁷

The preferential "eclipsed" configuration for Cp_2Fe^+ seems reasonable in light of the increases (over the Cp_2Fe derivatives) in the Fe-C and Fe-ring distances. The greatest remaining puzzle with respect to conformation is why ferrocene deriva-

tives are *staggered* in the solid state while ferrocene is *eclipsed* (and close to freely rotating) in the gas phase.

The longer Fe-C and Fe-ring distances in Cp_2Fe^+ suggest that the oxidation step ($Cp_2Fe \rightarrow Cp_2Fe^+$) removes an electron which is just slightly bonding with respect to iron-ring interactions. This is consistent with theoretical treatments of the molecular orbitals for ferrocene.²⁸⁻³⁰

Acknowledgment. This work was supported by the National Science Foundation.

Registry No. $(Cp_2Fe)_2As_4Cl_{10}O_2$, 75880-92-1; $AsCl_3$, 7784-34-1; Cp_2Fe , 102-54-5.

Supplementary Material Available: A table of observed and calculated structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

- (25) $\sigma(\text{ext})$ is an external estimate of the error on an individual bond distance obtained by the "scatter" of measurements of N equivalent bonds, viz., $\sigma(\text{ext}) = [\sum(d_i - \bar{d})^2 / (N - 1)]^{1/2}$. $\sigma(\text{av})$ is the esd on the average value calculated by $\sigma(\text{av}) = [\sum(d_i - \bar{d})^2 / (N^2 - N)]^{1/2}$.
- (26) Reference 7b gives Fe-C distances to only two decimal places. This value is the average of the 10 reported values and may well suffer from rounding errors.
- (27) Dunitz, J. D.; Orgel, L. E.; Rich, A. *Acta Crystallogr.* **1956**, *9*, 373.

- (28) Rettig, M. F. "N.M.R. of Paramagnetic Molecules, Principles and Applications"; LaMar, G. N., Horrocks, W. DeW., Holm, R. H., Eds.; Academic Press: New York, 1973; pp 217-242.
- (29) Lauher, J. W.; Hoffman, R. *J. Am. Chem. Soc.* **1976**, *78*, 1729-1742.
- (30) Schustorovich, E. M.; Dyatkina, M. E. *Dokl. Akad. Nauk SSSR* **1959**, *128*, 1234.

Contribution from the Department of Chemistry,
The University of Kansas, Lawrence, Kansas 66045

Crystal and Molecular Structure of a Macrocyclic Complex of Gold(III)

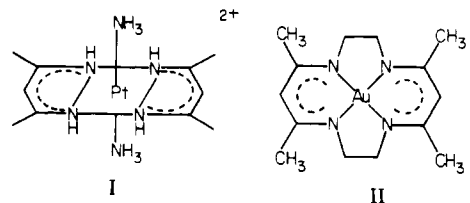
JONG-HO KIM and GROVER W. EVERETT, JR.*

Received June 26, 1980

(5,7,12,14-Tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato)gold(III) chloride dihydrate, prepared by condensation of $[Au(en)_2]Cl_3$ with 2,4-pentanedione, crystallizes in the monoclinic space group $C2/c$ with $a = 23.002$ (19) \AA , $b = 6.931$ (3) \AA , $c = 12.828$ (16) \AA , $\beta = 108.66$ (9) $^\circ$, and $Z = 4$. The structure was solved by Patterson and Fourier techniques and refined by least-squares calculations to a conventional R value of 0.037 for 2500 reflections. The gold atom is located at a crystallographic center of symmetry, and the macrocyclic cation is very nearly planar. Bond lengths within the β -diiminate rings indicate extensive π delocalization. The β -diiminate ring parameters are compared with those reported for related complexes.

Previous publications from this laboratory^{1,2} and others^{3,4} have shown that complexes containing β -diiminate chelate rings are formed when amine complexes of Pt(IV) and Au(III) react with β -diketones in aqueous base. The crystal structure of one of the Pt(IV) complexes, I, was reported earlier.¹ The six-membered β -diiminate rings were found to be planar, and the pattern of bond distances around the rings indicates complete delocalization of π electrons as shown in I.

The gold(III) β -diiminate complexes examined thus far have been prepared by condensation of $[Au(en)_2]Cl_3$ with a variety of β -diketones.² These are 14-membered, tetraaza ring, 12 π macrocyclic species exemplified by the cation (5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato)gold(III) hereafter referred to as II, which may be regarded as the parent member of the series.



Although a few complexes of the above macrocyclic ligand are known for first-row transition-metal ions,^{5,6} no structural details have been reported. In this paper we present the results of an X-ray crystallographic study of the chloride salt of II. Structural details of II are compared with those of related macrocyclic complexes.

Experimental Section

The macrocyclic cation II was prepared by the general method reported earlier,² and its chloride salt was precipitated by adding excess LiCl to the filtered reaction mixture. The product was recrystallized with use of acetone and diethyl ether. Slow evaporation of a 1-butanol

- (1) Brawner, S. A.; Lin, I. J. B.; Kim, J.-H.; Everett, G. W. *Inorg. Chem.* **1978**, *17*, 1304-1308.
- (2) Kim, J.-H.; Everett, G. W. *Inorg. Chem.* **1979**, *18*, 3145-3149.
- (3) Evans, I. P.; Everett, G. W.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1975**, 139-140.
- (4) Evans, I. P.; Everett, G. W.; Sargeson, A. M. *J. Am. Chem. Soc.* **1976**, *98*, 8041-8046.

- (5) Truex, T. J.; Holm, R. H. *J. Am. Chem. Soc.* **1971**, *93*, 285-286.
- (6) Truex, T. J.; Holm, R. H. *J. Am. Chem. Soc.* **1972**, *94*, 4529-4538.

Table I. Summary of Crystallographic Data for (5,7,12,14-Tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato)gold(III) Chloride Dihydrate

formula	AuN ₄ C ₁₄ H ₂₆ O ₂ Cl
<i>a</i> , Å	23.002 (19)
<i>b</i> , Å	6.931 (3)
<i>c</i> , Å	12.828 (16)
β , deg	108.66 (9)
cryst system	monoclinic
<i>V</i> , Å ³	1938 (3)
<i>Z</i>	4
<i>d</i> _{calcd} , g/cm ³	1.76
<i>d</i> _{obsd} , g/cm ³ ^a	1.87
space group	C2/c
cryst dimens, mm	0.20 × 0.33 × 1.4
cryst faces	(100), ($\bar{1}00$), (101), ($\bar{1}01$), (001), (001), (010), (010)
radiatn ^b	Mo K α ($\lambda = 0.71069$ Å)
abs coeff (μ), cm ⁻¹	79.5
scan rate, deg/min	2.0–20 (θ -2 θ)
scan range, deg	1.0 below K α_1 to 1.0 above K α_2
bkgd/scan time ratio	1.0
data collected	2 θ of 3–70°; $\pm h, -k, \pm l$
std reflctns	622, $\bar{3}\bar{3}\bar{1}$, $\bar{7}\bar{3}\bar{1}$
no. of independent reflctns	3937
no. of reflctns with <i>I</i> > 3 σ (<i>I</i>)	2500
no. of variables	106
error in observn of unit weight	2.17
<i>R</i>	0.037
<i>R</i> _w	0.063

^a Determined on the crystal used for data collection by flotation in CHBr₃ and CCl₄. ^b Graphite monochromated radiation.

solution of the final product yielded the crystals used for crystallography.

Subsequent to collection of the X-ray data, it was discovered that crystals grown in the above manner vary in density from crop to crop, probably as a result of having different numbers of water or 1-butanol molecules of crystallization. Dewan and Lippard recently noted a similar phenomenon for a Cu(II) complex and described its effects on elemental analyses and crystal density measurements.⁷ The crystal chosen for both film and diffractometer work was the best of those in the first preparation, and the remaining crystals were discarded prior to discovery of the above density variations. Thus for a realistic experimental value for the crystal density to be obtained, the crystal used for data collection was later removed from the glass fiber and used in the flotation experiments. The difference in observed and calculated densities (Table I) is likely the result of changes in composition of the crystal during the 8–10 month period in which the crystal was exposed to the atmosphere.

Collection and Reduction of the X-ray Data. A crystal which was approximately hexagonal in cross section and which appeared to be suitable for crystallographic work was mounted on a glass fiber with epoxy glue. The long axis of the crystal was approximately parallel to the fiber axis. Preliminary film data using zero and upper layer precession and Weissenberg techniques indicated a monoclinic crystal system with systematic absences for *hkl*, when *h* + *k* is odd, for *h0l*, when *l* is odd, and for *0k0*, when *k* is odd. This is consistent with only two space groups, *Cc* and *C2/c*.⁸

The crystal was then mounted on a Syntex P2, autodiffractometer. Standard Syntex programs were used to obtain the unit cell dimensions and orientation matrix by least-squares refinement of 2 θ , χ , and ϕ for 15 centered reflections. Data were collected by the θ -2 θ scan technique at ambient temperature. The three standard reflections, measured after every 97 reflections, showed a random variation of ~5%, indicating no significant decomposition of the crystal in the X-ray beam. Of a total of 3937 independent reflections collected, 2500 have *I* ≥ 3 σ (*I*) and were considered to be observed. Intensities and standard deviations are calculated by the equations $I = r(S - RB)$ and $\sigma^2(I) = r^2(S + R^2B)$, respectively, where *r* is the scan rate in deg/min, *S* is the total scan count, *R* is the scan to background

Table II. Final Atomic Positional Parameters^a

atom	<i>x</i>	<i>y</i>	<i>z</i>
Au	0.2500	0.2500	0.5000
Cl	0.4781 (3)	0.6947 (9)	0.4966 (7)
N(1)	0.2948 (2)	0.0397 (6)	0.4548 (4)
N(2)	0.1666 (2)	0.1564 (8)	0.4176 (4)
C(1)	0.3048 (12)	-0.2646 (13)	0.3624 (20)
C(2)	0.2662 (4)	-0.1056 (9)	0.3885 (5)
C(3)	0.2038 (4)	-0.1212 (8)	0.3432 (5)
C(4)	0.1566 (3)	-0.0029 (10)	0.3562 (5)
C(5)	0.0896 (4)	-0.0555 (14)	0.2971 (8)
C(6)	0.1207 (7)	0.3043 (33)	0.4347 (35)
C(7)	0.3598 (4)	0.0468 (14)	0.5022 (9)
O	0.4614 (2)	0.9879 (6)	0.3242 (3)
H(3) ^b	0.190	-0.250	0.300

^a Numbers in parentheses are estimated standard deviations in the least significant digits. ^b Proton bound to C(3); position not varied.

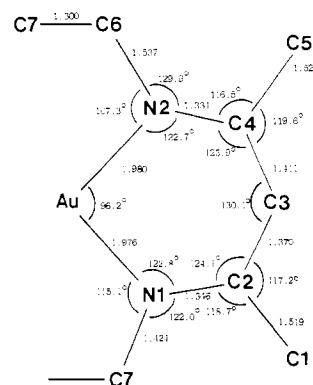


Figure 1. Bond distances and angles for the β -diiminate ring of cation II.

time ratio, and *B* is the background count. The data were corrected for absorption^{9,10} and for Lorentz and polarization effects.¹⁰ Maximum and minimum transmission coefficients are 0.2548 and 0.1007, respectively. Initial scale and overall temperature factors were determined from a Wilson plot.

Solution and Refinement of the Structure. The structure was solved by the heavy-atom method.¹¹ Initially the centrosymmetric space group *C2/c* was assumed. A three-dimensional Patterson synthesis revealed that the gold atom is on an inversion center at $1/4, 1/4, 1/2$. Subsequent Fourier syntheses revealed all the nonhydrogen atoms of the macrocyclic cation and the chloride ion. In addition, another heavy atom was found at a general position which was assumed to be oxygen from a molecule of water. Subsequent refinement verified this assumption. Three cycles of full-matrix, isotropic, least-squares refinement of all nonhydrogen atoms in space group *C2/c* resulted in a conventional *R* of 0.073 which dropped to 0.051 after three additional cycles during which Au and Cl were varied anisotropically and anomalous scattering factors were used for these atoms. During refinement the quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. Atomic scattering factors of Cromer and Waber¹² were used.

After several additional cycles of full-matrix, least-squares refinement in which all atoms were varied anisotropically, a difference Fourier map was generated. The latter revealed significant electron density near C(1) and C(6). Temperature factors for these atoms were also much larger than those of other atoms. These observations indicated that the space group is incorrect and/or that the structure is disordered. A peak at the position expected for the C(3) proton was clearly evident, but other hydrogen atoms were not detected with

(7) Dewan, J. C.; Lippard, S. J. *Inorg. Chem.* **1980**, *19*, 2079–2082.

(8) Henry, N. F. M.; Lonsdale, K., Eds. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1965; Vol. I.

(9) de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014–1018.

(10) Computer programs used for data reduction were written by Professor B. Lee of this department.

(11) Programs used for solution and refinement of the structure are local modifications of FORDAF by A. Zalkin and of ORFLS and ORFFE-II by W. Busing, K. Martin, and H. Levy. C. K. Johnson's ORTEP-II was used for the structural drawing. All computations were carried out on a Honeywell 66/60 computer located on campus.

(12) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104–109.

Table III. Final Atomic Thermal Parameters ($\times 10^4$) and Their Estimated Standard Deviations^a

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Au	332 (3)	378 (5)	382 (3)	19 (1)	125 (2)	-12 (1)
Cl	1020 (38)	877 (25)	1099 (43)	100 (37)	467 (34)	55 (41)
N1	683 (34)	486 (25)	531 (28)	187 (22)	297 (25)	12 (22)
N2	390 (26)	676 (35)	459 (25)	-79 (23)	94 (20)	-1 (27)
C1	1900 (220)	960 (97)	1340 (150)	433 (71)	960 (160)	-301 (61)
C2	946 (53)	477 (33)	477 (34)	8 (32)	313 (36)	14 (27)
C3	950 (53)	491 (36)	499 (35)	-49 (34)	254 (36)	1 (28)
C4	719 (41)	641 (39)	400 (28)	-278 (31)	91 (27)	55 (28)
C5	760 (55)	1345 (77)	1048 (72)	-571 (52)	-193 (50)	38 (59)
C6	469 (72)	2460 (180)	3680 (400)	582 (94)	780 (160)	190 (240)
C7	508 (46)	975 (62)	1241 (70)	-8 (38)	271 (44)	-492 (54)
O	914 (31)	831 (32)	584 (27)	225 (22)	356 (24)	175 (23)

^a The form of the anisotropic temperature factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

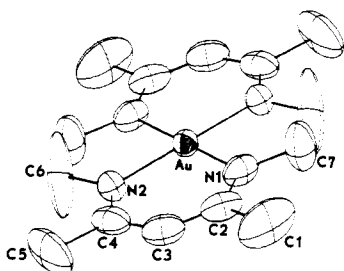


Figure 2. ORTEP drawing of the macrocyclic cation II showing the numbering scheme. Thermal ellipsoids are drawn at the 50% level.

certainty. A number of attempts at refinement were subsequently made both in space group $C2/c$ and in Cc with use of a double precision matrix inversion routine and by varying both the positions and occupancies of the disordered atoms. For example, C(6) was placed at positions both above and below the AuN_4 plane and assigned partial occupancies which were allowed to vary. These attempts were unsuccessful, however. In many cases the refinement did not converge but rather oscillated. When it did converge, the R factor was not significantly better than the original structure, and large temperature factors remained. Since our interests lie primarily in the basic structure of the β -diiminate chelate ring, further efforts to resolve the disorder were not made. A similar situation was reported by Gordon, Peng, and Goedken during solution of the structure of a Ni(II) macrocyclic complex of related structure.¹³

Several final cycles of full-matrix, least-squares refinement in which H(3) was fixed at its observed position (with an isotropic temperature factor of 6.5) and all other atoms were varied anisotropically resulted in the R values shown in Table I. The largest shift of any parameter during the last cycle was 5% of σ except for the disordered C(6) and its neighbor C(7) for which maximum shifts were 20% and 12% of σ , respectively. A final difference Fourier map was featureless except for a peak having $2.6 e/\text{\AA}^3$ at the disordered C(6) atom and some residual electron density near the Au atom ($\pm 1.5 e/\text{\AA}^3$).

Final atomic positions and thermal parameters are given in Tables II and III, respectively. Bond lengths and angles are listed in Table IV and illustrated in Figure 1. Table V, containing observed and calculated structure factors, is available as supplementary material.

Results and Discussion

The cation (Figure 2) has the macrocyclic structure expected from results of earlier characterization by IR, NMR, and mass spectra.² The gold atom is at a crystallographic center of symmetry, and the entire cation is very nearly planar. The maximum deviation of any nonhydrogen atom from the least-squares plane of the entire cation is 0.025\AA (C(3)). Neither the chloride ion nor the water molecules are sufficiently close to the cation for any significant interaction.

The β -diiminate chelate ring dimensions have some features in common with those of the analogous bidentate ligand in

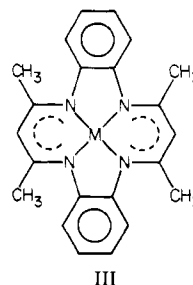
Table IV. Bond Lengths and Selected Bond Angles^a

Bond Lengths, \AA			
Au-N(1)	1.976 (4)	C(2)-C(1)	1.519 (15)
Au-N(2)	1.980 (5)	C(2)-C(3)	1.370 (10)
N(1)-C(2)	1.346 (8)	C(3)-C(4)	1.411 (10)
N(1)-C(7)	1.424 (9)	C(4)-C(5)	1.528 (10)
N(2)-C(4)	1.334 (8)	C(3)-H(3)	1.045 (6)
N(2)-C(6)	1.537 (18)		
Bond Angles, Deg			
N(1)-Au-N(2)	96.2 (2)	N(1)-C(2)-C(1)	118.7 (12)
Au-N(1)-C(2)	122.8 (5)	C(1)-C(2)-C(3)	117.2 (11)
Au-N(1)-C(7)	115.1 (4)	C(2)-C(3)-C(4)	130.1 (6)
C(2)-N(1)-C(7)	122.0 (6)	N(2)-C(4)-C(3)	123.9 (6)
Au-N(2)-C(4)	122.7 (4)	N(2)-C(4)-C(5)	116.5 (7)
Au-N(2)-C(6)	107.3 (11)	C(3)-C(4)-C(5)	119.6 (7)
C(4)-N(2)-C(6)	129.9 (12)	C(2)-C(3)-H(3)	113.0 (6)
N(1)-C(2)-C(3)	124.1 (6)	C(4)-C(3)-H(3)	116.4 (7)

^a Estimated standard deviations in the least significant digits are given in parentheses.

complex I,¹ but significant differences result from the presence of the ethylene bridges in the macrocyclic complex. In both structures the β -diiminate ring shows little deviation from planarity. The Au-N bonds are $\sim 0.02 \text{\AA}$ shorter than the Pt-N bonds, and the N(1)-Au-N(2) angle is 6° larger than that found in the platinum complex. This larger N(1)-Au-N(2) angle is compensated for by smaller angles at N(1) and N(2) and a larger angle at C(3) inside the six-membered ring of the gold complex. In the macrocyclic structure, C-N bonds are longer by $\sim 0.02 \text{\AA}$, but the near equivalence of independent C-N and C-C bonds in each structure indicates substantial π delocalization. The observed C-N bond lengths of 1.31 - 1.34\AA in I and II may be compared with those (1.26 - 1.28\AA) reported recently for localized C=N bonds in a neutral, β -diimine ligand.¹⁴

Crystal structure determinations have been carried out for a number of β -diiminate ring macrocyclic complexes of type III by Goedken and co-workers,¹⁵⁻¹⁹ where M is a first-row



(13) Gordon, G. C.; Peng, S. M.; Goedken, V. L. *Inorg. Chem.* **1978**, *17*, 3578-3586.

(14) DeHaven, P. W.; Goedken, V. L. *Inorg. Chem.* **1979**, *18*, 827-831.
 (15) Weiss, M. C.; Bursten, B.; Peng, S. M.; Goedken, V. L. *J. Am. Chem. Soc.* **1976**, *98*, 8021-8031.

transition-metal ion. These complexes generally have a saddle shape which is attributed to steric interactions between the aromatic rings and the methyl groups. A planar structure was found in one case where the methyls are absent.¹⁷ Bond lengths found for the β -diiminate portions of the macrocyclic ligand in complex II are very close to those reported for complexes III. For example, C \rightarrow N, C \rightarrow C, and C—CH₃ bond lengths for

III fall in the ranges 1.31–1.35 Å, 1.38–1.41 Å, and 1.49–1.52 Å, respectively.^{15–19} Bond angles for II are also close to those observed for III except for the Au—N \rightarrow C angles which are 2–6° smaller.

Acknowledgment. We are indebted to Drs. K. Mertes, B. Lee, and R. Sheldon of this department for valuable advice and to Dr. Lee for use of his library of computer programs. We also thank the University of Kansas for a generous allocation of computer time.

Registry No. II·Cl·2H₂O, 76037-14-4.

Supplementary Material Available: Table V containing observed and calculated structure factor amplitudes (16 pages). Ordering information is given on any current masthead page.

- (16) Goedken, V. L.; Peng, S. M.; Molin-Norris, J.; Park, Y. *J. Am. Chem. Soc.* **1976**, *98*, 8391–8400.
 (17) Weiss, M. C.; Gordon, G.; Goedken, V. L. *Inorg. Chem.* **1977**, *16*, 305–310.
 (18) Weiss, M. C.; Goedken, V. L. *Inorg. Chem.* **1979**, *18*, 274–279.
 (19) Weiss, M. C.; Goedken, V. L. *Inorg. Chem.* **1979**, *18*, 819–826.

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

Preparations and ¹H, ¹³C, and ³¹P Nuclear Magnetic Resonance Studies of Some *N,N*-Dialkyldiselenocarbamate Complexes and Their Phosphine Derivatives. X-ray Crystal Structure of Pt(Se₂CN(*i*-Bu)₂)₂

WIE-HIN PAN, JOHN P. FACKLER, JR.,* and H.-W. CHEN

Received August 14, 1980

A convenient synthesis of CSe₂ is reported which can be used to prepare dialkyldiselenocarbamates. The ¹H, ¹³C, and ³¹P NMR spectra of about 25 derivatives containing the metal ions Zn(II), Ni(II), Pd(II), Pt(II), Pt(IV), and Co(III) are reported. The single-crystal X-ray structure of monoclinic Pt(Se₂CN(*i*-Bu)₂)₂ ($a = 6.736(1)$ Å, $b = 12.357(2)$ Å, $c = 15.496(4)$ Å, $\beta = 99.03(2)^\circ$) establishes the coordination geometry to be the same as that found¹ for the Pt(S₂CNEt₂)₂ analogue. The average Pt–Se distance is 2.427(3) Å, an increase of ~ 0.11 Å over the Pt–S distance, similar to the increase observed for Ni–Se over Ni–S.

While the chemistry of the dithiocarbamates¹ began back in the middle 1800s, the chemistry of the diselenocarbamates is of more recent origin. The preparation of CSe₂ was reported in as early as 1936 by Grimm and Metzger,² but it was not until in 1961 that Barnard and Woodbridge³ described the first preparations of the sodium salts and zinc and copper complexes of dialkyldiselenocarbamic acids, using CSe₂ as one of the starting materials. Apparently, this delay in the development of the chemistry of the diselenocarbamates is due to the toxicity⁴ and unpleasant odor associated with CSe₂ (and selenium compounds in general^{4,5}), rendering it difficult to handle. It was also noted^{3,6} that unlike CS₂, CSe₂ polymerizes readily, particularly in the presence of base, making it useless for the preparation of the diselenocarbamate salt by reaction with amines. An additional drawback is the generally low yield encountered in the preparation of CSe₂ by using the early methods of Grimm and Metzger² and Ives et al.⁶

The development^{7,8} of ⁷⁷Se NMR has prompted our studies of the selenium analogues of metal dithiocarbamates. Much spectroscopic data (IR,^{9,10} UV–vis¹⁰) as well as a few crystal

structures¹¹ of *N,N*-dialkyldiselenocarbamate complexes have been reported. There is, however, a scarcity of NMR data¹² on these types of complexes. In the course of our study, some interesting multinuclear (¹H, ¹³C, and ³¹P) NMR results have been obtained. Also a small scale (~ 20 g) convenient synthesis of CSe₂, with yields upward of 80%, has been devised. This method is a simplified version of the one reported by Henriksen and Kristiansen¹³ for preparing CSe₂ on a larger scale (800 g). The structure of Pt(Se₂CN(*i*-Bu)₂)₂, synthesized from CSe₂, also is described here.

Experimental Section

Preparation of Compounds. Reagent grade solvents were used unless otherwise stated. The compounds MCl₂(PR₃)₂ (M = Ni, Pd, Pt)^{14,15} and *cis*-Pt(CH₃)₂(PPh₃)₂¹⁶ were prepared according to literature methods. K₂PdCl₄ and K₂PtCl₄ were prepared from the respective metals, the former following the method of Kauffman and Tsai¹⁷ for Na₂PdCl₄ and the latter according to Brauer.¹⁸ All chemical analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. (Table I).

Carbon Diselenide. Figure 1 is a diagram of the apparatus used. Grey Se powder (16–22 g) in a quartz boat (14 × 1.5 cm) is placed

- (1) Coucouvanis, D. *Prog. Inorg. Chem.* **1970**, *11*, 234–371; **1979**, *26*, 302–451.
 (2) Grim, H. G.; Metzger, H. *Chem. Ber.* **1936**, *69*, 1356.
 (3) Barnard, D.; Woodbridge, E. T. *J. Chem. Soc.* **1961**, 2922.
 (4) Sax, N. I. "Dangerous Properties of Industrial Materials", 2nd ed.; Reinhold: New York, 1963; p 575.
 (5) "Organic Selenium Compounds: Their Chemistry and Biology"; Klayman, D. L., Günther, W. H. H., Eds.; Wiley-Interscience: New York, 1973.
 (6) Ives, D. J. G.; Pittman, R. W.; Wardlaw, W. J. *Chem. Soc.* **1947**, 1080.
 (7) Pan, W.-H.; Fackler, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 5783. Harris, R. K.; Mann, B. E. "NMR and the Periodic Table"; Academic Press: New York, 1978; Chapter 12.
 (8) Fackler, J. P.; Pan, W.-H. *J. Am. Chem. Soc.* **1979**, *101*, 1607.
 (9) Jensen, K. A.; Krishnan, V. *Acta Chem. Scand.* **1969**, *24*, 1088.

- (10) (a) DeFilipo, D.; Deplan, P.; Diaz, A.; Trogu, E. F. *Inorg. Chim. Acta* **1976**, *17*, 139. (b) DeFilipo, D.; Deplano, P.; Devillanova, F.; Trogu, E. F. *Ibid.* **1976**, *17*, 199. (c) Mannooussakis, G. E.; Tsipis, C. A.; Chirstophides, A. G. *Inorg. Chem.* **1973**, *12*, 3015.
 (11) Bonamico, M.; Dessy, G. *J. Chem. Soc. A* **1971**, 264.
 (12) Tanaka, T.; Sonoda, N. *Inorg. Chem.* **1971**, *10*, 2337.
 (13) Henriksen, L.; Kristiansen, E. S. S. *Int. J. Sulfur Chem. Part A* **1972**, *2*, 133.
 (14) Jenkins, J. M.; Shaw, B. L. *J. Chem. Soc. A* **1966**, 770.
 (15) Cousmaker, C. R.; Hely-Hurchinson, M.; Mellor, J. R.; Sutton, L. E.; Venanzi, L. M. *J. Chem. Soc.* **1961**, 2705.
 (16) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1959**, 705.
 (17) Kauffman, G. B.; Tsai, J. H.-S. *Inorg. Synth.* **1966**, *8*, 234.
 (18) Brauer, G. "Handbook of Preparative Inorganic Chemistry"; Academic Press: New York, 1965; Vol. 2, p 1572.