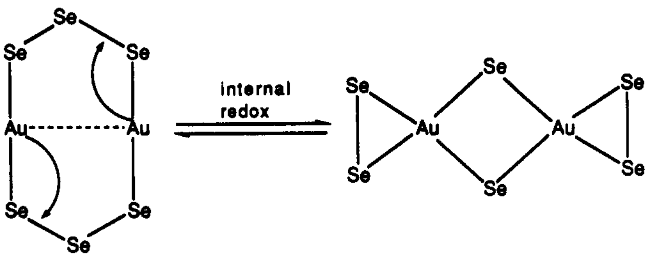
Scheme I



Au^+/Te_2^{2-} system (i.e. $[Au_2(Te_2)_2]^{2-}$),[13] where the Te–Te distance is 2.781 Å, closer to the Au–Au distance of 2.908 Å. In anticipation that a symmetrical molecule such as $[Au_2(Se_3)_2]^{2-}$ or $[Au_2(Se_4)_2]^{2-}$ might form with higher concentration of longer polyselenides in solution, we used Se_4^{2-} instead of the original Se_2^{2-} and Se_3^{2-}. Unexpectedly, the isolated molecule, III, contains a Se_2^{2-} unit bridging the two gold atoms while a Se_4^{2-} ligand is adopted on the other side. The fact that the more symmetric compound $(Ph_4P)_2[Au_2(Se_x)_2]$ (x = 3, 4) does not form is intriguing, in view of the apparent stability of a sulfur analogue, $[Au_2(S_4)_2]^{2-}$.[11] The reason for the preferential formation of I–III might rest with the stability of the $Au_2(Se_2)$ unit. It might be reasonably speculated that if indeed $[Au^I_2(Se_x)_2]^{2-}$ (x = 3, 4) formed in solution, it could be susceptible to internal redox electron transfer between Au(I) and Se–Se bonds according to Scheme I. This is similar to that thought to occur in the formation of $[(Ph_3P)_2N]_2[Au^{III}_2Se_2(Se_4)_2]$.[8] However, it is more difficult to reduce the Se–Se bonds in Se_2^{2-} than those in Se_3^{2-} or Se_4^{2-}. The species $[Au^{III}_2Se_2(Se_x)_2]^{2-}$ (x = 2, 3) formed by the internal electron transfer may not be favored under such conditions due to the small size of the Se_x^{2-} ligand, which cannot span the square-planar gold coordination site. The work presented here suggests that the Au(I) vs Au(III) interplay is largely dominated by the size of the Se_x^{2-} ligands. This is an exception to the widely accepted view that ligand preferences of the metal ions are more important in determining structure than the sizes of the Se_x^{2-} ligands used. This is certainly true with divalent and trivalent ions such as Cd^{2+}, Ni^{2+}, and In^{3+}.[14]

At this point, it is relevant to discuss the polymeric polyselenide $KAuSe_5$.[15] The structure consists of dimeric one-dimensional $[AuSe_5]_n^{n-}$ anionic chains with linearly coordinated Au(I) atoms being bridged by long open chains of Se_5^{2-} [8] ligands. The Au(I)–Au(I) distance between two chains is 2.95 Å. It is interesting that oxidation of this compound to a Au(III) species does not occur despite the existence of Se_5^{2-} ligands. However, the compound was prepared in molten Se_x^{2-}, in which different equilibria might be operable, and it was found that indeed slight deviations from the optimum Au/Se_x^{2-} ratio *do* induce redox chemistry and formation of Au(III) compounds.[15]

Compounds I and II have identical far-IR spectra showing absorptions at 265 and 236 cm^{-1}. The spectrum of compound III is similar, but an additional peak appears at 257 cm^{-1}. The strongest peak in all spectra is at 236 cm^{-1}. The absorptions at 265 and 257 cm^{-1} can be attributed to Se–Se stretching vibrations,[7] while those at 236 cm^{-1} most likely arise from Au–Se stretching vibrations.

The isolation of two Au(I) polyselenide compounds in this work and the Au(III) species in the previous report[8] as a function of Se_x^{2-} length and counterion size attests to the vacillating nature of redox chemistry between Au(I)/Au(III) and polyselenide ligands and suggests that considerably more chemistry would be possible in this system. Analogous redox chemistry with corresponding S_x^{2-} and Te_x^{2-} ligands remains to be seen.[16]

Acknowledgment. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. We are grateful to the National Science Foundation for a Presidential Young Investigator Award.

Supplementary Material Available: Tables of crystal structure analyses, atomic coordinates of all atoms, and anisotropic and isotropic thermal parameters of all non-hydrogen atoms, and calculated and observed powder patterns for I–III (24 pages); listings of calculated and observed ($10F_o/10F_c$) structure factors for I–III (54 pages). Ordering information is given on any current masthead page.

---

(16) Huang, S.-P.; Kanatzidis, M. G. Work in progress.

Contribution from the Department of Chemistry,
Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka 560, Japan

Mixed-Metal Chloro Sulfido Cluster Complex of Molybdenum and Platinum, $[Mo_3Pt_2S_4Cl_4(PEt_3)_6]$

Taro Saito,*,† Toshio Tsuboi, Yoshimichi Kajitani,
Tsuneaki Yamagata, and Hideo Imoto†

Received January 30, 1991

In our recent publication, syntheses of mixed-metal chloro sulfido and chloro selenido complexes of molybdenum and nickel were reported.[1] They were prepared by the reaction of $[Mo_3X_4Cl_4(PEt_3)_3(MeOH)_2]$ (X = S, Se)[2] with $Ni(cod)_2$ (cod = 1,5-cyclooctadiene). In the present study, another excellent building block compound, $Pt(cod)_2$,[3] was reacted with the same trinuclear molybdenum complex, and the mixed-metal cluster complex $[Mo_3Pt_2S_4Cl_4(PEt_3)_6]$ (**1**) with an unexpected structure was obtained.

Experimental Section

Synthesis. A solution of $Pt(cod)_2$[4] (0.18 g, 0.44 mmol) in THF (20 mL) was mixed with a toluene solution of triethylphosphine (0.4 mL, 0.66 mmol) and stirred for 30 min. To the resulting deep yellow solution was added $[Mo_3S_4Cl_4(PEt_3)_3(MeOH)_2]$ (0.23 g, 0.22 mmol). The solution was stirred at room temperature, and its color gradually changed to green. After 8 h, the solvent, triethylphosphine, and cyclooctadiene were removed under reduced pressure, and the residue was washed with hexane (2 × 7 mL). The soluble component was extracted with ether (3 × 40 mL), and removal of ether formed a green powder. Recrystallization of the solid from THF–hexane gave dark green needles (0.18 g). Anal. Calcd for $C_{38}H_{94}Cl_4Mo_3O_{0.5}P_6Pt_2S_4$: C, 26.96; H, 5.60; Cl, 8.38; Mo, 17.00; Pt, 23.04. Found: C, 27.06; H, 5.40; Cl, 8.32; Mo, 17.5; Pt, 23.4. ^{195}Pt NMR (in 25% toluene-d_8; 106.95 MHz; Na_2PtCl_6 as an external reference): δ −4560 (dd with satellites due to a Pt–Pt coupling of 700 Hz;[5] J_{Pt-P} = 4410, 3100 Hz). The complex is air-sensitive and decomposed gradually in the crystalline state and rapidly in solution when exposed to air.

X-ray Structure Determination. Single crystals of **1** were sealed in glass capillary tubes under dinitrogen for the X-ray measurements. The intensity data were collected by a Rigaku AFC-5 diffractometer equipped with a Rotaflex rotating anode X-ray generator. The data showed the structure had the *C*-centered orthorhombic symmetry, and the observed systematic absences indicated the space group *Cmca* or *C2ca*. The structure could be solved only by *C2ca*, and the setting of the cell was transformed so that the structure had the standard symmetry *Aba*2. The positions of metal atoms were determined by direct methods (MULTAN78), and other non-hydrogen atoms were located on the Fourier maps. Though it was not possible to distinguish chlorine and sulfur atoms from the X-ray data, we assigned all bridging ligand atoms to sulfur for the following reasons. (1) The observed bond distances of terminal ligands with molybdenum atoms are longer than those of the bridging ligands, and the Mo–S distances are generally shorter than the Mo–Cl distances. (2) Terminal sulfido ligands are rare while terminal chlorine atoms are common. (3) It is unlikely that the central part $[Mo_3S_4]$ of the starting complex rearranges during the preparation reaction. The THF molecule was found on the 2-fold axis as broad Fourier peaks, and it was treated as a rigid C_5 pentagon with a C–C distance of 1.52 Å. All carbon atoms were treated isotropically while all other non-hydrogen atoms were treated anisotropically. In the final full-matrix least-squares refinements, hydrogen atoms were included at calculated positions (C–H = 0.92 Å) with a fixed thermal parameter. If the enantiomeric structure was as-

---

† Present address: The Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo, 113, Japan.

0020-1669/91/1330-3575$02.50/0

Table I. Crystal Data for $[Mo_3Pt_2S_4Cl_4(PEt_3)_6]\cdot 0.5THF$

formula	$C_{38}H_{94}Cl_4Mo_3O_{0.5}P_6Pt_2S_4$	D_{calcd}, g cm^{-3}	1.792
fw	1693.06	T, K	298
space group	*Aba*2	λ(Mo Kα), Å	0.709 26
a, Å	28.506 (6)	no. of obsd reflcns	3484 (>5σ)
b, Å	20.289 (3)	μ, cm^{-1}	55.3
c, Å	21.714 (6)	abs cor factors	1.00–1.41
V, Å^3	12558 (4)	R, R_w[a]	0.069, 0.037
Z	8		

[a] $w = 1/\sigma^2(|F_o|)$.

Table II. Atomic Parameters (×10^3) and (Equivalent) Isotropic Thermal Parameters (Å^2 × 10^3) for $[Mo_3Pt_2S_4Cl_4(PEt_3)_6]\cdot 0.5THF$

atom	x/a	y/b	z/c	U_{iso}
Pt(1)	76.11 (4)	257.35 (6)	281.78	5.1 (1)
Pt(2)	215.85 (4)	417.17 (6)	418.63 (9)	4.8 (1)
Mo(1)	143.2 (1)	338.2 (1)	355.0 (2)	4.6 (2)
Mo(2)	112.7 (1)	222.4 (1)	400.0 (1)	4.5 (2)
Mo(3)	177.0 (1)	295.7 (1)	463.3 (1)	4.6 (2)
Cl(1)	107.3 (3)	442.0 (4)	313.6 (4)	8.5 (8)
Cl(2)	186.8 (4)	350.4 (5)	262.8 (4)	9.6 (9)
Cl(3)	130.5 (3)	108.5 (4)	377.5 (4)	6.6 (6)
Cl(4)	249.9 (3)	247.7 (4)	494.3 (4)	6.7 (6)
S(1)	64.8 (2)	310.2 (4)	371.2 (4)	5.4 (6)
S(2)	140.6 (2)	397.5 (4)	446.2 (4)	5.2 (5)
S(3)	189.3 (2)	246.0 (4)	367.5 (4)	4.8 (5)
S(4)	110.0 (3)	249.7 (4)	501.8 (4)	6.2 (6)
P(1)	21.9 (3)	314.1 (5)	223.5 (5)	8.1 (8)
P(2)	110.0 (3)	186.1 (5)	215.9 (5)	7.3 (7)
P(3)	211.9 (3)	532.5 (4)	412.1 (8)	10.2 (8)
P(4)	290.0 (3)	390.8 (5)	390.4 (5)	7.7 (7)
P(5)	33.4 (3)	167.8 (4)	425.2 (6)	7.6 (7)
P(6)	185.3 (4)	343.9 (5)	573.4 (4)	7.6 (8)
C(1)	35 (2)	354 (3)	159 (3)	17 (2)
C(2)	70 (2)	411 (3)	158 (2)	17 (2)
C(3)	−22 (1)	266 (2)	184 (2)	11 (1)
C(4)	−55 (1)	236 (2)	236 (2)	16 (2)
C(5)	−12 (1)	374 (2)	270 (2)	12 (2)
C(6)	−53 (2)	397 (4)	234 (3)	32 (4)
C(7)	86 (1)	101 (2)	213 (2)	9 (1)
C(8)	37 (1)	92 (2)	189 (2)	12 (2)
C(9)	105 (1)	200 (2)	133 (2)	9 (1)
C(10)	137 (1)	259 (2)	117 (2)	13 (2)
C(11)	172 (1)	168 (2)	228 (2)	9 (1)
C(12)	199 (1)	127 (2)	179 (2)	9 (1)
C(13)	251 (1)	577 (2)	451 (2)	14 (2)
C(14)	246 (2)	569 (2)	516 (2)	14 (2)
C(15)	153 (1)	561 (2)	436 (2)	9 (1)
C(16)	143 (2)	633 (3)	445 (3)	20 (2)
C(17)	225 (2)	576 (3)	338 (2)	16 (2)
C(18)	200 (2)	558 (3)	284 (3)	24 (3)
C(19)	324 (2)	439 (3)	351 (3)	22 (3)
C(20)	306 (1)	448 (2)	288 (2)	10 (1)
C(21)	337 (1)	387 (2)	454 (2)	14 (2)
C(22)	345 (1)	443 (2)	495 (2)	15 (2)
C(23)	299 (1)	313 (2)	349 (2)	9 (1)
C(24)	347 (1)	292 (2)	324 (2)	10 (1)
C(25)	12 (1)	120 (2)	362 (2)	10 (1)
C(26)	−38 (2)	86 (2)	367 (2)	15 (2)
C(27)	−23 (1)	221 (2)	438 (2)	13 (2)
C(28)	−19 (1)	263 (2)	493 (2)	15 (2)
C(29)	31 (2)	111 (2)	492 (2)	14 (2)
C(30)	66 (2)	73 (2)	516 (2)	18 (2)
C(31)	202 (2)	277 (3)	641 (2)	17 (2)
C(32)	180 (2)	221 (4)	642 (3)	28 (4)
C(33)	241 (1)	394 (2)	578 (2)	9 (1)
C(34)	255 (2)	428 (2)	639 (2)	13 (2)
C(35)	147 (2)	410 (3)	599 (3)	19 (2)
C(36)	100 (2)	401 (3)	598 (3)	26 (3)
C(37)	0 (0)	0 (0)	−75 (2)	20 (3)
C(38)	25 (1)	49 (1)	−34 (2)	19 (2)
C(39)	16 (1)	30 (1)	32 (2)	22 (3)

sumed, the refinement gave a much higher R value ($R = 0.083$, $R_w = 0.047$).

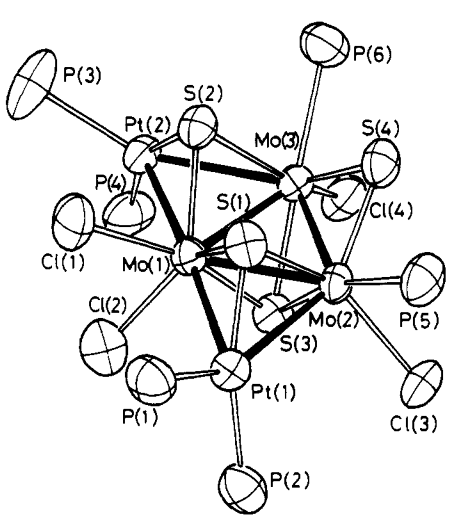


Figure 1. ORTEP drawing showing the framework of the molecular structure of $[Mo_3Pt_2S_4Cl_4(PEt_3)_6]$. Carbon and hydrogen atoms are omitted. Thermal ellipsoids are drawn at the 50% probability level.

Table III. Selected Bond Distances (Å) and Angles (deg) for $[Mo_3Pt_2S_4Cl_4(PEt_3)_6]\cdot 0.5THF$

Pt(1)–Mo(1)	2.979 (3)	Mo(2)–S(4)	2.281 (9)
Pt(1)–Mo(2)	2.860 (3)	Mo(3)–S(2)	2.340 (8)
Pt(2)–Mo(1)	2.961 (3)	Mo(3)–S(3)	2.338 (8)
Pt(2)–Mo(3)	2.870 (3)	Mo(3)–S(4)	2.285 (9)
Mo(1)–Mo(2)	2.689 (4)	Mo(1)–Cl(1)	2.506 (10)
Mo(1)–Mo(3)	2.684 (4)	Mo(1)–Cl(2)	2.371 (10)
Mo(2)–Mo(3)	2.732 (4)	Mo(2)–Cl(3)	2.415 (9)
Pt(1)–S(1)	2.241 (8)	Mo(3)–Cl(4)	2.395 (9)
Pt(2)–S(2)	2.262 (8)	Pt(1)–P(1)	2.305 (11)
Mo(1)–S(1)	2.331 (8)	Pt(1)–P(2)	2.250 (10)
Mo(1)–S(2)	2.318 (8)	Pt(2)–P(3)	2.347 (12)
Mo(1)–S(3)	2.303 (8)	Pt(2)–P(4)	2.264 (10)
Mo(2)–S(1)	2.330 (8)	Mo(2)–P(5)	2.578 (11)
Mo(2)–S(3)	2.345 (8)	Mo(3)–P(6)	2.592 (11)

Mo(1)–Pt(1)–Mo(2)	54.8 (1)	Pt(2)–Mo(3)–Mo(2)	123.8 (1)
Mo(1)–Pt(2)–Mo(3)	54.8 (1)	Mo(1)–Mo(3)–Mo(2)	59.5 (1)
Pt(1)–Mo(1)–Pt(2)	174.9 (1)	Pt(1)–S(1)–Mo(1)	81.3 (3)
Pt(1)–Mo(1)–Mo(2)	60.4 (1)	Pt(1)–S(1)–Mo(2)	77.5 (3)
Pt(1)–Mo(1)–Mo(3)	121.4 (1)	Mo(1)–S(1)–Mo(2)	70.5 (2)
Pt(2)–Mo(1)–Mo(2)	121.9 (1)	Pt(2)–S(2)–Mo(1)	80.6 (3)
Pt(2)–Mo(1)–Mo(3)	60.9 (1)	Pt(2)–S(2)–Mo(3)	77.2 (3)
Mo(2)–Mo(1)–Mo(3)	61.1 (1)	Mo(1)–S(2)–Mo(3)	70.4 (2)
Pt(1)–Mo(2)–Mo(1)	64.8 (1)	Mo(1)–S(3)–Mo(2)	70.7 (2)
Pt(1)–Mo(2)–Mo(3)	124.1 (1)	Mo(1)–S(3)–Mo(3)	70.7 (2)
Mo(1)–Mo(2)–Mo(3)	59.4 (1)	Mo(2)–S(3)–Mo(3)	71.4 (2)
Pt(2)–Mo(3)–Mo(1)	64.3 (1)	Mo(2)–S(4)–Mo(3)	73.5 (3)

The reflection data were collected at the University of Tokyo, and calculations were performed at the Research Center for Protein Engineering, Osaka University. The crystallographic data are given in Table I. Atomic coordinates are listed in Table II.

Results and Discussion

Structure. The X-ray structure of complex **1** crystallized with THF molecules is illustrated in Figure 1. Interatomic distances and angles are given in Table III.

The structure is nearly symmetric with respect to the plane that passes through the central molybdenum Mo(1), S(3), and two chlorine atoms bonded to Mo(1) and intersects the Mo(2)–Mo(3) bond. The molecule has a planar Mo_3Pt_2 framework, which contains a Mo_3 triangle in the center connected with a platinum atom on two edges. The same geometry of the metals has been

---

(1) Saito, T.; Kajitani, Y.; Yamagata, T.; Imoto, H. *Inorg. Chem.* **1990**, *29*, 2951.

(2) Saito, T.; Yamamoto, N.; Yamagata, T.; Imoto, H. *Chem. Lett.* **1987**, 2025.

(3) Adams, R. D.; Arafa, I.; Chen, G.; Lii, J.-C.; Wang, J.-G. *Organometallics* **1990**, *9*, 2350.

(4) Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 271.

(5) Though the two platinum atoms are chemically equivalent, they are magnetically nonequivalent due to the existence of ^{31}P nuclei.

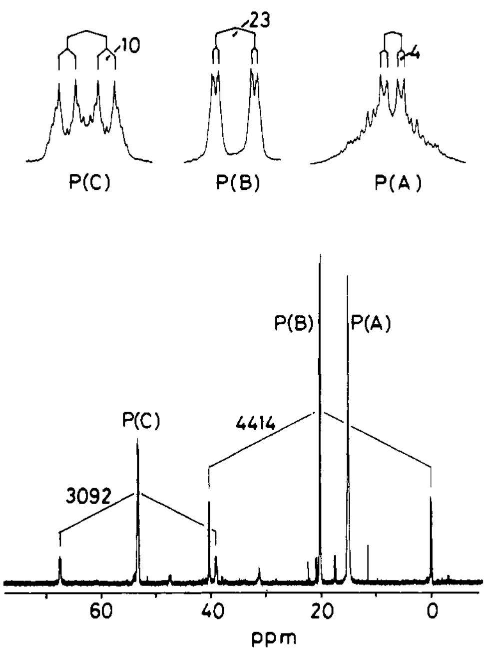


Figure 2. ^{1}H-decoupled ^{31}P NMR spectrum of $[Mo_3Pt_2S_4Cl_4(PEt_3)_6]\cdot0.5THF$ in 25% toluene-d_8 (109.25 MHz; reference, 85% H_3PO_4). Numbers in the figure are observed coupling constants in hertz.

reported for several carbonyl cluster complexes.[6] The two μ_3-sulfido ligands S(1) and S(2) capping the Mo_2Pt triangle are on the same side of the Mo_3Pt_2 plane while S(3) capping the Mo_3 is on the other. The fourth sulfido ligand, S(4), is bridging the unique unshared edge of the Mo_3 triangle. Both of the platinum atoms are slightly shifted (0.12 Å) from the plane determined by the three molybdenum atoms to the side where S(3) exists. All of the molybdenum atoms have five coordinating ligands ("Cl_2S_3" for Mo(1), and "ClS_3P" for Mo(2) and Mo(3)). The platinum atoms have a μ_3-sulfido ligand and two terminal phosphine ligands.

The configuration of the starting Mo_3 complex is kept in the central part of **1**. Three μ_2-sulfido ligands in the Mo_3 complex correspond to S(1), S(2), and S(4) in **1**. In both the starting Mo_3 complex and **1**, all phosphine ligands bonded to the molybdenum atoms are approximately trans to the μ_3-sulfido ligand on the Mo_3 triangle.

The Mo–Mo distances are in the range 2.68–2.73 Å, which shows bonding interaction between the molybdenum atoms (calculated bond order: 0.73).[7] On the other hand, the Mo–Pt distances (2.86–2.98 Å) indicate that the Mo–Pt bonds are weak (calculated bond order: 0.29). The Mo_3 triangle in **1** is not regular: the distance Mo(2)–Mo(3) is longer by 0.04–0.05 Å than the distances Mo(1)–Mo(2) and Mo(1)–Mo(3). Similar deformation of the Mo_3 triangle has been observed in $[Mo_3Ni_2S_4Cl_4(PEt_3)_5]$ where the basal Mo–Mo distance is longer by 0.04–0.06 Å than other Mo–Mo distances.[1] These deformations may be attributed to the larger electron donation from the two d^{10} metal atoms to the central molybdenum atom than from the other two molybdenum atoms.

The number of the cluster valence electrons in this cluster complex is 68, which is 6 electrons fewer than that of the square-pyramidal nickel derivative that has five phosphine ligands.[1] The small number is due to the bonding mode of the chloro ligands, which are all terminal, and may be ascribed to the general trend in the cluster compounds that platinum derivatives have fewer valence electrons than would be expected on the basis of the polyhedral skeletal electron pair theory.[8]

NMR Spectra. The ^{31}P NMR spectrum of **1** measured in 25% toluene-d_8 is shown in Figure 2. There are three resonances at 15.1 (A), 20.3 (B), and 53.2 ppm (C). This is consistent with the X-ray structure showing three pairs of equivalent phosphines {P(1),P(3)}, {P(2),P(4)}, and {P(5),P(6)}. Peak A, which shows no coupling with ^{195}Pt, is assigned to the triethylphosphines coordinated to the molybdenum atoms, {P(5),P(6)}. Peaks B and C accompany satellite peaks due to ^{31}P–^{195}Pt couplings of 3092 and 4414 Hz, respectively, and they are assigned to the phosphorus atoms bonded with the platinum atoms.[9] The splittings of the main peaks originate from ^{31}P–^{31}P couplings; J(AB) = 4.0 Hz, J(AC) = 10.0 Hz, and J(BC) = 23.0 Hz. The fine couplings between the equivalent nuclei further modify the spectrum since the six phosphorus atoms constitute an AA′MM′XX′ spin system. They were, however, too small to be determined unequivocally.

Acknowledgment. We thank Dr. A. Kobayashi for the X-ray data collection. The financial support from Ministry of Education, Science and Culture of Japan (Grant-in-Aid for Scientific Research No. 63430010) and the gift of triethylphosphine from Nippon Chemical Co. Ltd. are gratefully acknowledged.

Supplementary Material Available: Tables of full crystallographic details, anisotropic thermal parameters, hydrogen atom parameters, and complete bond distances and angles (7 pages); a table of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

---

(6) (a) Michael, D.; Mingos, P.; May, A. S. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH Publishers: New York, 1990; pp 38–41. (b) Adams, R. D.; Chen, G.; Lii, J.-C.; Wu, W. *Inorg. Chem.* **1991**, *30*, 1007.

(7) The relation between the metal-metal distance with the number of valence electrons in the transition-metal cluster compounds with π-donor ligands was extensively discussed in ref 7c. (a) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 239. (b) Teatum, E.; Gschneider, K.; Waber, J. quoted in Pearson, W. B. The *Crystal Chemistry and Physics of Metals and Alloys*; Wiley: New York, NY, 1972; p 151. (c) Corbett, J. D. *J. Solid State Chem.* **1981**, *37*, 335.

(8) Mingos, D. M. P.; Johnston, R. L. *Struct. Bonding* **1987**, *68*, 29.

(9) Further unambiguous assignments of peaks B and C are not possible at present. We can, however, tentatively assign peak B with a smaller coupling with ^{195}Pt ($J_{\text{P-Pt}}$ = 3092 Hz) to {P(1),P(3)} which has a longer P–Pt bond distance (2.33 Å on the average), and peak C ($J_{\text{P-Pt}}$ = 4414 Hz) to {P(2),P(4)}, (P–Pt distance: 2.26 Å on the average).

Contribution from the Department of Chemistry,
University of Wyoming, Laramie, Wyoming 82071

Barium Binding to Carboxylate Residues: Synthesis and Structure of a New Form of Barium Malonate

Derek J. Hodgson* and R. Owen Asplund

Received November 27, 1990

It has been suggested that the presence of the modified amino acid residue γ-carboxyglutamate (Gla) in place of glutamate (Glu) in prothrombin and other blood coagulation proteins is due to the the availability of a dicarboxylate in Gla rather than a simple carboxylate function; the dicarboxylate would bind preferentially to calcium rather than magnesium, thereby allowing the protein to discriminate between the two metals.[1] The binding of these metal ions to carboxylates has been extensively studied by Einspahr and Bugg,[2] who note that a simple carboxylate (e.g. Glu) can bind the calcium (or, by extension, barium) in either a unidentate or a bidentate manner. In a dicarboxylate (e.g. mal, Gla) there is an additional mode in which the barium binds to two oxygen atoms from the two different carboxylate groups. This mode, which is only available to a dicarboxylate like malonate (mal), is sometimes

---

(1) Williams, R. J. In *Calcium Binding Proteins and Calcium Function*; Wasserman, R. H., et al., Eds.; Elsevier: New York, 1977; pp 1–12.

(2) Einspahr, H.; Bugg, C. E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**, *B37*, 1044–1052.