In case I, the two methyl groups A and B within each isopropyl moiety are diastereotopic by internal comparison and become enantiotopic when pyramidal inversion is rapid on the nmr time scale. On the other hand, in case II, the two isopropyl groups, A and B, are diastereotopic by external comparison and become homotopic when rotation is rapid on the nmr time scale. Evidently, the collapse of the 8-line spectrum to a quartet at temperatures above 110° could correspond to the interchange of the environments of A and B by either process. However, that pyramidal inversion is the observed process may be deduced from two independent observations.

First, in case I the two interconverting isomers are enantiomers and are thus equally populated, whereas in case II they are diastereomers and are not expected to exist in a 1:1 ratio, nor in a ratio that is independent of temperature and solvent. The observation that the two sets of signals derived from A and B are of equal intensity over the whole temperature range and are independent of solvent thus speaks for case I.[9]

Second, the acetyl methyl groups in case I are enantiotopic, in case II diastereotopic, and under conditions of fast exchange become homotopic in both processes. One would thus expect, in the slow exchange limit, two resonances for case II and only one for case I. One resonance was observed,[10] and again the result is only compatible with case I.[11–14]

Ancillary evidence for the correctness of the assignment is provided by calculation. The CNDO/2 scheme has recently been parametrized[15] to reproduce, with a high degree of accuracy, barriers to pyramidal inversion for a wide variety of systems containing first- and second-row elements. Use of this scheme results in a barrier of 22 kcal/mol for acetyldimethylphosphine, in good agreement with that obtained for **1** by dnmr. Support for the accuracy of the experimental barrier derives from the observed coalescence of the $-OCH_3$ signals from the diastereomers of methyl (*O*-methylmandelyl)phenylphosphine (**2**). Coalescence (at *ca.* 100°, $\Delta\delta_{AB}$ 0.24 ppm) is between two uncoupled, unequally populated sites and a first-order rate constant is readily calculated.[16] The $\Delta G^{\ddagger}$ values determined for the interconversion of the diastereomers of **2** (in a 40:60 ratio) are 19.1 and 19.3 kcal/mol.

The low inversion barrier found for acylphosphines may be thought of as arising from enhanced $(p-p)\pi$ conjugation in the planar transition state, relative to the pyramidal ground state, of the phosphorus lone pair with the carbonyl group, producing, in effect, the contributing dipolar structures presented in Figure 1. The effect on the phosphorus–carbonyl torsional barrier is evidently considerably less than the corresponding effect in amides.

The contrast between the geometry (and conformational barriers) of amides and acylphosphines is accounted for by the significantly higher "intrinsic" inversion barrier of acyclic phosphines (30–36 kcal/mol)[4] as compared to amines (4–8 kcal/mol);[17] in structures differing only in the identity of the inverting center (N *vs.* P), it is far easier to flatten the nitrogen than the phosphorus pyramid.[18]

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(9) The utilizable temperature range was −75 to 90°. Below and above these temperatures broadening was too severe. The solvent for the low-temperature study (−100 to 45°) was $CF_2Cl_2$ while that for the higher temperatures (45–150°) was 1-bromonaphthalene. A 1:1 ratio was also observed at 45° in $C_6D_6$.

(10) The conditions were as in ref 9, except that the acetyl methyl remained as a sharp signal to 150°, the highest temperature employed.

(11) Nmr and ir evidence for conformational isomerism in acylphosphines have been presented,[12] but neither the nature of the interconversion (rotation *vs.* inversion) nor the barrier height was determined. The ir spectrum of trifluoroacetyldiphenylphosphine presented in this work[12] is not in accord with that published by Lindner and Kranz.[13]

(12) R. G. Kostyanovskii, V. V. Yakshin, and I. I. Chervin, *Dokl. Akad. Nauk SSSR*, 188, 366 (1969), and references cited therein.

(13) E. Lindner and H. Kranz, *Chem. Ber.*, 101, 3438 (1968).

(14) An interpretation based on the interconversion of rotational isomers in a pyramidally stable 1 is ruled out by the observed simplicity of the pmr spectrum.

(15) A. Rauk, J. D. Andose, W. G. Frick, R. Tang, and K. Mislow, unpublished work.

(16) H. Shanan-Atidi and K. H. Bar-Eli, *J. Phys. Chem.*, 74, 961 (1970).

(17) A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem., Int. Ed. Engl.*, **9**, 400 (1970).

(18) *Cf.* also, W. Egan, R. Tang, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 1442 (1970); R. D. Baechler and K. Mislow, *ibid.*, **93**, 773 (1971).

(19) National Aeronautics and Space Administration Fellow, 1969–1970.

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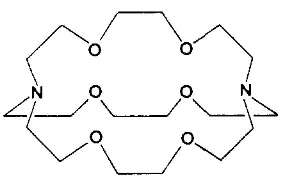
*Received December 17, 1970*

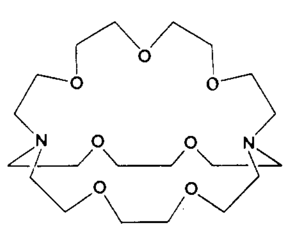
## Crystal Structures of Two Barium Cryptates

*Sir:*

New types of metal–cation complexes known as cryptates[1,2] have recently been the subject of considerable interest. The crystal and molecular structures of ligand I and of the corresponding rubidium cryptate have already been reported.[3,4] We wish now to describe the structures of two complexes formed by barium thiocyanate with the ligands I and II. We started this study in order to compare the structures of alkali and alkaline-earth metal cryptates of different stabilities[5] and also to show the role of the water molecules present in the barium complexes of this type.



I: $C_{18}H_{36}N_2O_6$



II: $C_{20}H_{40}N_2O_7$

Suitable crystals of $[(I)Ba^{2+}][SCN^-]_2\cdot H_2O$ (denoted by A) and $[(II)Ba^{2+}][SCN^-]_2\cdot 2H_2O$ (denoted by B) were prepared by slow evaporation of methanol–butanol solutions of the ligands and barium thiocyanate in the ratio 1:1. Analytical results agree with the formulas given for the compounds.

A crystallizes in the orthorhombic system with $a$ = 37.728 (11), $b$ = 19.525 (5), $c$ = 15.303 (3) Å; $\rho_{obsd}$ = 1.57 ± 0.02, and $\rho_{calcd}$ = 1.54 g cm$^{-3}$ based on 16 formula species per cell. Diffraction symmetry and

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(1) B. Dietrich, J. M. Lehn, and J. P. Sauvage, *Tetrahedron Lett.*, 2885 (1969).

(2) B. Dietrich, J. M. Lehn, and J. P. Sauvage, *ibid.*, 2889 (1969).

(3) B. Metz, D. Moras, and R. Weiss, *Proc. Int. Conf. Coord. Chem.*, *13th, 1970*, **2**, 85 (1970).

(4) B. Metz, D. Moras, and R. Weiss, *Chem. Commun.*, 217 (1970).

(5) J. M. Lehn and J. P. Sauvage, to be published.

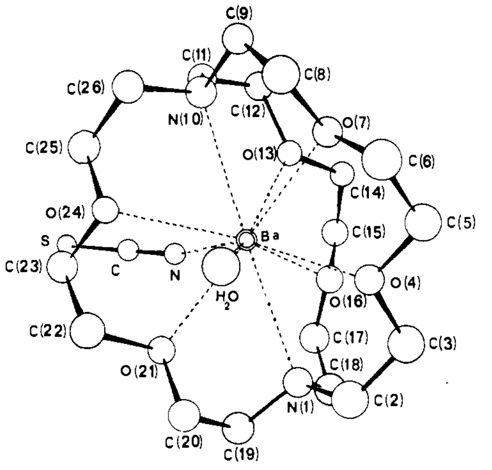


Figure 1. A view of the complex cations $[(I)Ba(SCN)(H_2O)]^+$ present in A.

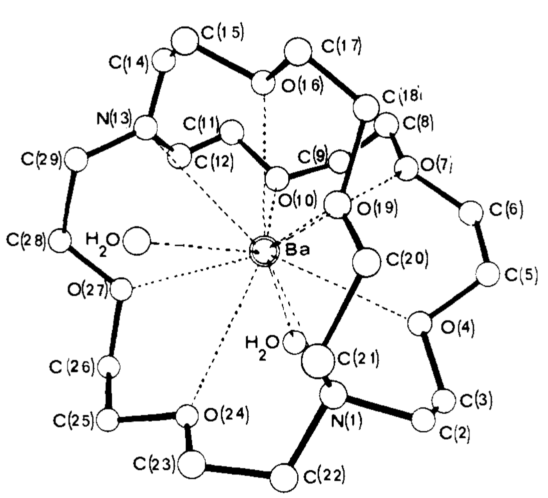


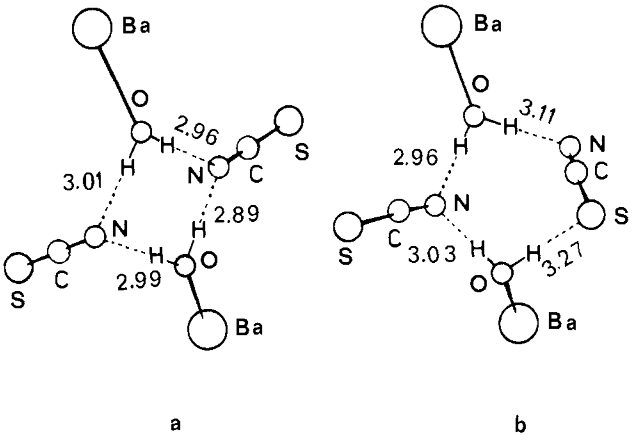
Figure 2. A view of the complex cation $[(II)Ba(H_2O)_2]^{2+}$ present in B.

extinctions correspond to the orthorhombic space group *Pbca* ($D_{2h}^{15}$) with two formula species per asymmetric unit. Three-dimensional intensity data were collected with monochromated Mo K$\alpha$ radiation (quartz plate) on a Picker four-circle automatic diffractometer. A total of 5827 independent nonzero reflections was retained ($2\theta_{max} = 50°$). Final block diagonal matrix least-squares refinement of the structure yielded a standard residual, $R_1 = 0.079$, and a weighted residual, $R_2 = 0.084$. Anisotropic thermal parameters were used for the two barium atoms and the 12 atoms of the thiocyanate groups. All other atoms were included with isotropic thermal parameters.

Diffraction symmetry and extinctions of B correspond to the monoclinic space group $P2_1/c$ ($C_{2h}^5$) with $a = 11.58$ (1), $b = 16.03$ (1), $c = 19.56$ (2) Å; $\beta = 121.15$ (20)°; $\rho_{obsd} = 1.50 \pm 0.03$, and $\rho_{calcd} = 1.52$ g cm$^{-3}$ for $Z = 4$. A total of 2923 independent and observable reflections was measured with monochromated Mo K$\alpha$ radiation (silicium plate) on a Pailred diffractometer ($2\theta_{max} = 55°$). The structure was solved by conventional Patterson, Fourier, and least-squares refinement techniques. Anisotropic thermal parameters were used for all nonhydrogen atoms. The final conventional $R_1$ factor $= 0.035$ and weighted $R_2 = 0.043$; the positions of the hydrogen atoms were calculated and located on a difference Fourier synthesis.

The structure of the cations in the unit cell of A, $[(I)Ba(SCN)(H_2O)]^+$, is represented in Figure 1. The structure of the complex cation in B, $[(II)Ba(H_2O)_2]^{2+}$, is represented in Figure 2.

The conformations of the ligands I and II in these cations are *in–in*[6] with the metal ions located within the molecular cage. In $[(I)Ba(H_2O)(SCN)]^+$ the metal is bonded to the eight heteroatoms of I, an oxygen atom of a water molecule, and the nitrogen atom of a thiocyanate group. The polyhedron defined by the eight heteroatoms of I is a distorted bicapped trigonal prism. Two rectangular faces of the prism are capped by the oxygen atom of the water molecule and the nitrogen atom of the thiocyanate group bonded to the barium. The $Ba^{2+} \cdots O$ and $Ba^{2+} \cdots N$ distances range, respectively, from 2.74 (1) to 2.88 (1) Å (mean value, 2.81 Å) and 2.94 (1) to 3.00 (1) Å (mean value, 2.98 Å). The $Ba^{2+} \cdots OH_2$ distance is 2.86 (1) Å and the $Ba^{2+} \cdots (NCS)^-$ distance is 2.88 (1) Å. The two complex cations of the asymmetric unit are linked together by a hydrogen bond system represented schematically in Figure 3a.



a b

Figure 3. The hydrogen bond system present in A (a) and in B (b).

In B the barium is surrounded by the nine heteroatoms of II and two water molecules. The undecacoordination polyhedron around barium is very similar to that found in thorium nitrate pentahydrate.[7–9] The $Ba^{2+} \cdots O$ and $Ba^{2+} \cdots N$ distances range from 2.80 (1) to 3.09 (1) Å (mean value, 2.91 Å) and 3.09 (1) to 3.18 (1) Å (mean value, 3.13 Å). The $Ba^{2+} \cdots OH_2$ distances found are 2.81 (1) and 2.88 (1) Å. Similar $Ba^{2+} \cdots O$ distances were found recently in the barium salt of the antibiotic X-537A.[10] The complex cations are linked in chains by a hydrogen bond system represented schematically in Figure 3b.

As all the oxygen and nitrogen atoms are directed toward the inside of the cage, the $Ba^{2+}$ ions in both A and B are enclosed by a hydrophobic shell and are

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[6] H. E. Simons and C. H. Park, *J. Amer. Chem. Soc.*, **90**, 2428 (1968).

[7] E. L. Muetterties and C. M. Wright, *Quart. Rev., Chem. Soc.*, **21**, 109 (1967).

[8] T. Ueki, A. Zalkin, and D. H. Templeton, *Acta Crystallogr.*, **20**, 836 (1966).

[9] J. C. Taylor, M. H. Mueller, and R. L. Hitterman, *ibid.*, **20**, 842 (1966).

[10] S. M. Johnson, J. Herrin, S. J. Liu, and I. C. Paul, *J. Amer. Chem. Soc.*, **92**, 4428 (1970).

still partially hydrated or in strong interaction with the anion. Similar structural features are present in the $Ba^{2+}$ salt of antibiotic X-537A[10] in which, however, the hydrophobic exterior is large in comparison with that of ligands I and II.

The structure of A shows that ligand I can only partially remove the hydration sphere of barium whereas it generally replaces completely the hydration spheres of the alkali metal ions. In the solid-state structures of the alkali metal cryptates of ligand I, the cation is located within the molecular cage and is surrounded only by the eight heteroatoms. The metal ion does not interact appreciably with the anion or with water molecules when the latter are present. In all the compounds studied so far, metal–anion or metal–$H_2O$ distances are greater than 3.5 Å.[4,11]

The structural data suggest also that the selectivity of ligand I for the $Ba^{2+}$ ion is higher than that of ligand II. A higher coordination number is observed for the cation in B but as a result of the geometrical constraints the distances between the cation and the heteroatoms are greater and hence the energy contribution per dipole is smaller (see the mean values given for the barium–oxygen and barium–nitrogen distances).

**Acknowledgment.** We thank Professor J. M. Lehn for supplying the compounds.

(11) B. Metz, D. Moras, and R. Weiss, to be published.

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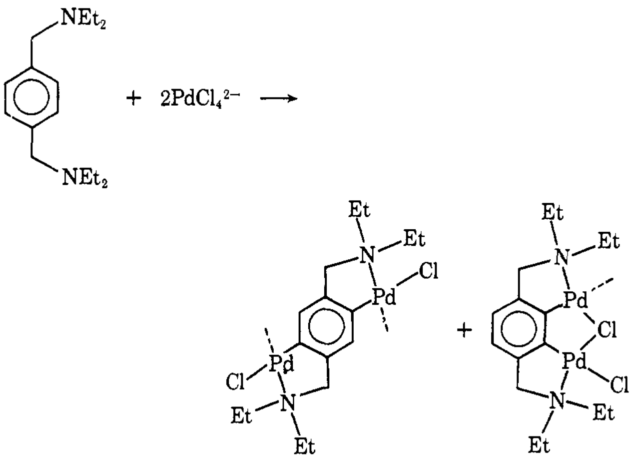
## Dipalladiobenzenes

*Sir:*

Numerous compounds containing a transition metal $\sigma$ bonded to an aromatic ring have been reported in recent years.[1] These compounds encompass a variety of transition metals and also different types of substitution on the benzene ring. However, in no instance has the bonding of more than one transition metal to the same benzene ring been accomplished. We now wish to report the synthesis and characterization of 1,2-, 1,3-, and 1,4-dipalladiobenzenes which constitute the first such examples. These compounds were prepared by the ortho-palladation reaction[2-4] and characterized by elemental analysis, nmr spectroscopy, and conversion to diverse 1,3-diketonato and pyridine derivatives.

The reaction of *N,N,N′,N′*-tetraethyl-*p*-xylylenediamine with tetrachloropalladate ion in 95% aqueous methanol in the presence of 1 equiv of a hindered tertiary amine readily gave a mixture of dimetalated products. Of these, the insoluble polymeric 1,4-dipalladio derivative I was isolated by filtration, while the soluble 1,2-dipalladio derivative II was precipitated by diluting the filtrate with water. The I:II ratio was about 7:3.



I II

The 1,4-dipalladio compound, I, was converted to the monomeric bisacetylacetonato derivative,[5] III, mp 240–242° dec, the nmr spectrum of which indicated substitution of two aromatic hydrogens and the presence of two acetylacetonato ligands per molecule: $\tau$ 3.07 (s, aromatic H), 4.66 (s, acetylacetonato CH), 6.00 (s, benzylic $CH_2$), 7.03 (m, two overlapping quadruplets, $J = 7.0$) (ethyl $CH_2$), 7.96 (s), 8.05 (s, both acetylacetonato $CH_3$), and 8.47 (t, ethyl $CH_3$, $J = 7.0$) in a 1:1:2:4:3:3:6 ratio.

The 1,2-dipalladio derivative II was sufficiently soluble in halocarbons to permit purification and analysis.[5] Its nmr spectrum indicated substitution of two aromatic hydrogens and $C_{2v}$ symmetry for the molecule: $\tau$ 3.87 (s, aromatic H), 6.38 (s, benzylic $CH_2$), ~7.5 (center of complex multiplet, ethyl $CH_2$), and (t, ethyl $CH_3$, $J = 7.0$) in a 1:2:4:6 ratio. The assignment of structure II rather than I for this compound rests not only on its higher solubility[6] but also on chemical evidence which indicates one of the chlorines to be less reactive than the other. Thus, the reaction of II with aqueous pyridine gave the cation IV, isolated as the hexafluorophosphate,[5] mp 220–225° dec. Compound IV still contained one bridging chlorine and its nmr spectrum was consistent with $C_{2v}$ symmetry: $\tau$ 1.75 (m, pyridine 2-H), 2.6 (m, pyridine 4-H), 3.0 (m, pyridine 3-H), 3.80 (s, aromatic H), 6.31 (s, benzylic $CH_2$), (m, two overlapping quadruplets), 7.6 (ethyl $CH_2$), and 8.82 (t, $J = 7.0$, ethyl $CH_3$) in the correct 2:1:2:1:2:4:6 ratio. Simple 2-(dialkylaminomethyl)-phenylpalladium(II) chlorides, as well as their 1,4- and 1,3-dipalladio analogs, react with aqueous pyridine, invariably giving cations containing two pyridines per palladium.

While the distance between the two palladium atoms in II is too great for a Pd–Pd bond,[7] the two atoms are close enough so that 1,3-diketonate substituents interfere with each other, causing distortion of the

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(1) G. W. Parshall and J. J. Mrowca, *Advan. Organometal. Chem.*, 7, 157 (1968).

(2) A. C. Cope and E. C. Friedrich, *J. Amer. Chem. Soc.*, **90**, 909 (1968).

(3) G. W. Parshall, *Accounts Chem. Res.*, 3, 139 (1970).

(4) G. E. Hartwell, R. V. Lawrence, and M. J. Smas, *Chem. Commun.*, 912 (1970).

(5) Satisfactory elemental analyses and molecular weights were obtained for this and other compounds reported here.

(6) A compound such as II with one rather than two *intermolecular* chlorine bridges would be expected to be more soluble.

(7) Taking the Pd–C distance found in the 2-phenylazophenylpalladium analog [D. L. Weaver, *Inorg. Chem.*, **9**, 2250 (1970)] and assuming normal bond distances and angles in the phenyl ring, the Pd–Pd distance turns out to be abut 3.4 Å, considerably greater than the bonding distance of 2.64 Å based on covalent radii.