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^{129}I Mössbauer Spectroscopic Study of 2:3 Molecular Complexes of Triphenylphosphine Sulfide-Iodine and Acridine-Iodine

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The ^{129}I Mössbauer effect has been applied to investigate 2:3 molecular complexes of triphenylphosphine sulfide-iodine and acridine-iodine. The Mössbauer spectra indicate the presence of three unequivalent iodine sites (I_A, I_B, and I_C), as expected from the crystallographic data of these complexes. The iodine atom (I_A) coordinating to the sulfur or nitrogen atom of each donor molecule is more positively charged than that of the 1:1 molecular complex containing the same donor atom. This result can be interpreted in terms of the covalency of the $S\cdots I_A$ or $N\cdots I_A$ bond. The degrees of charge transfer in the 2:3 complexes are close to those in the 1:1 complexes, and the transferred charges are mainly localized on the terminal iodine atoms (I_B). The iodine molecule (I_C) cross-linked to two I_B atoms has a slightly negative charge, consistent with the bond distance of the molecule. The iodine moieties of these complexes are very similar to the structure of I_8^{2-} in Cs_2I_8.

The iodine molecule is known to be a typical electron acceptor and to form molecular or charge-transfer complexes with various electron-donor molecules such as amines, ethers, and thioethers. Many of these complexes usually have a 1:1 stoichiometry in the solid phase, consisting of a linear orientation of the iodine molecule with the donor atom. However, triphenylphosphine sulfide (TPPS)[1] and acridine (AC)[2] form 2:3 molecular complexes with the iodine molecule in the solid state, although these donors form 1:1 complexes with iodine monobromide. The crystallographic data of the triphenylphosphine sulfide-iodine (2TPPS-3I_2) complex suggest that two iodine molecules are bonded to each sulfur atom of two TPPS molecules, resulting in a nearly linear $S\cdots I_A$-I_B arrangement; another iodine molecule is cross-linked to two terminal iodine atoms (I_B) with a Z-shaped structure (Fig. 1).[3] The six iodine atoms of the complex lie in one plane. The intermolecular $S\cdots I_A$ bond distance (2.69 Å) is considerably shorter than the sum of the respective van der Waals radii, whereas the intramolecular I_A-I_B bond disance (2.86 Å) is longer than that of the free iodine molecule. The corresponding bond distances for the usual 1,4-dithiane-iodine complex having a similar $S\cdots I_A$-I_B configuration have been reported as 2.867 Å for the $S\cdots I_A$ bond and 2.787 Å for the I_A-I_B bond.[4] This comparison of the bond distances for both complexes suggests that the charge-transfer interaction of the unusual 2:3 iodine complex is stronger than that of usual 1:1 iodine complex containing the same donor atom.

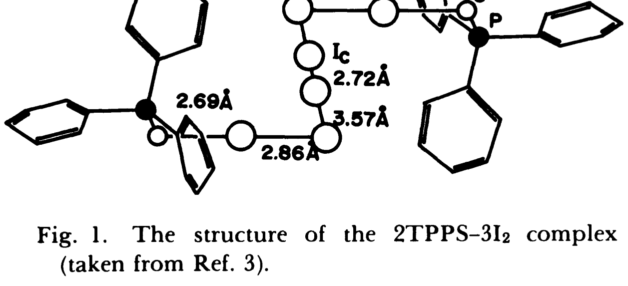

Fig. 1. The structure of the 2TPPS-3I_2 complex (taken from Ref. 3).

Recently, Uchida[5] has revealed the crystal structure of the acridine-iodine (2AC-3I_2) complex, in which the configuration of the iodine atoms is very similar to that of 2TPPS-3I_2. This 2:3 complex is apparently not the ionic compound formulated as $[(AC)_2I]^+I_5^-$, predicted from the low-frequency vibrational spectra.[2] Ichiba et al.[6] previously measured the ^{129}I Mössbauer spectrum of the acridine-iodine complex at 85 K. The analysis of the spectrum with two unequivalent iodine atoms (1:1 type complex) did not give a completely satisfactory result, suggesting the existence of three unequivalent iodine atoms in the complex.

It is of interest to estimate the charge densities on the iodine atoms in the unusual 2:3 iodine complexes of TPPS and AC, in comparison with those in the usual 1:1 iodine complexs of thioethers and amines. The Mössbauer spectroscopy of ^{129}I is favorable for this purpose, since the charge density and the charge distribution on the iodine atom can be directly derived from the such Mössbauer parameters as the quadrupole coupling constant (e^2Qq) and its sign, the asymmetry parameter (η), and the isomer shift (δ). In the present work, the ^{129}I Mössbauer spectra of the 2TPPS-3I_2 and 2AC-3I_2 complexes were measured and the electronic structure on each iodine atom could be determined. The nature of the charge-transfer bond for these 2:3 complexes is discussed in comparison with that for 1:1 complexes of thioether-iodine and amine-iodine.

Experimental

The complexes were prepared on a small scale using radioactive ^{129}I (99% enriched) obtained from the New

England Nuclear Co. as Na ^{129}I in a Na_2SO_3 solution. Molecular iodine, prepared by H_2O_2 oxidation of an acidified solution of NaI, was extracted with carbon tetrachloride or chloroform. Each iodine solution was thoroughly washed with water and passed through a Teflon filter to eliminate any slight amount of water. The 2TPPS-$3I_2$ complex was prepared by adding a solution of a stoichiometric amount of TPPS in carbon tetrachloride to the iodine solution of the same solvent. A purple-red crystalline product was collected by filtration and air-dried. The mole ratio was determined for a complex prepared with nonradioactive (natural) iodine by elemental analysis. Found: C, 31.7; H, 2.5; I, 56.7%. Calculd for $2(C_6H_5)_3PS$-$3I_2$: C, 32.0, H, 2.2; I, 56.4%. A brown crystalline complex of 2AC-$3I_2$ was prepared in chloroform using a procedure similar to that for the 2TPPS-$3I_2$ complex. The iodine content was determined to be 67.4% by means of iodometry. Calculd for $2(C_{13}H_9N)$-$3I_2$: I, 68.0%. The thicknesses of the absorber samples, mounted in Teflon sample holders, were in the range of 20 to 30 mg ^{129}I cm^{-2}.

The ^{66}Zn^{129}Te Mössbauer source was prepared by irradiation of 150 mg ^{66}Zn ^{128}Te compound at a thermal neutron fluence rate of 2×10^{13} n cm^{-2} s^{-1} for 1 h in the Kyoto University Reactor (KUR). The source, about 10 mCi in radioactivity initially, was immediately used for the measurement since the half life of ^{129}Te is very short (70 min). The Mössbauer measurement was carried out in the transmission geometry by cooling the source and the absorber to 16 K with a closed-cycle helium refrigerator. For the 2AC-$3I_2$ complex the spectra were measured at 78 K in addition to 16 K in order to make a comparison with the previous spectrum.[6] The Mössbauer spectrometer was calibrated using an iron foil spectrum.

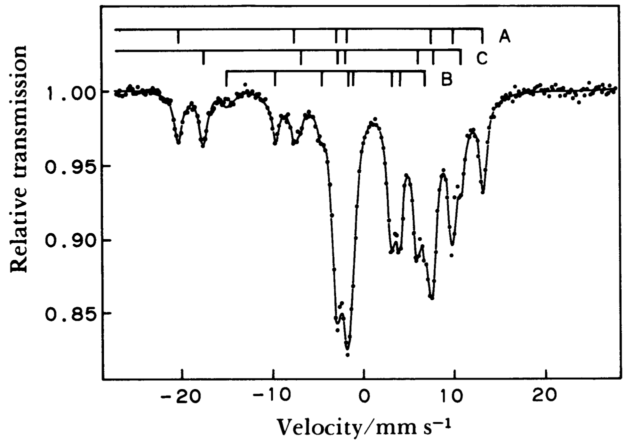

Fig. 2. ^{129}I Mössbauer spectrum of the 2TPPS-$3I_2$ complex at 16 K.

Results and Discussion

The Mössbauer spectra of the 2TPPS-$3I_2$ and 2AC-$3I_2$ complexes are shown in Figs. 2 and 3. The top (a)

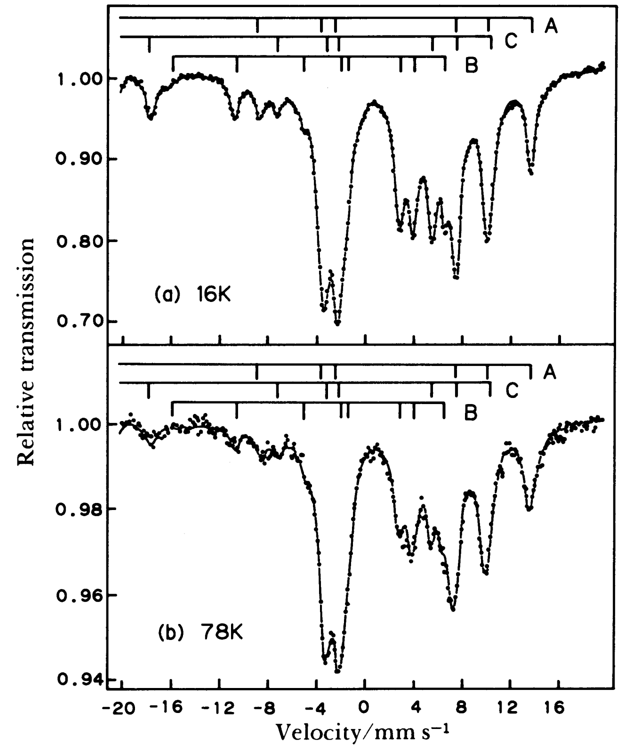

Fig. 3. ^{129}I Mössbauer spectra of the 2AC-$3I_2$ complex at (a) 16 K and (b) 78 K.

Table 1. ^{129}I Mössbauer Parameters for the 2:3 Molecular Complexes of 2TPPS-$3I_2$ and 2AC-$3I_2$ and the 1:1 Molecular Complexes of 1,4-Dithiane-$2I_2$ and Pyridine-I_2

		e^2Qq[a)] / MHz	η	δ[b)] / mm s^{-1}	U_p[c)]	h_p[d)]	Ref.
2TPPS-$3I_2$ (16 K)	I_A	-2618 ± 20	0.0	1.47 ± 0.04	1.14	1.34	
	I_B	-1221 ± 20	0.20 ± 0.05	0.38 ± 0.04	0.53	0.61	
	I_C	-2219 ± 20	0.0	0.88 ± 0.04	0.97	0.95	
2AC-$3I_2$ (16 K)	I_A	-2937 ± 20	0.0	1.58 ± 0.04	1.28	1.41	
	I_B	-1326 ± 20	0.17 ± 0.05	0.38 ± 0.04	0.58	0.61	
	I_C	-2276 ± 20	0.0	0.96 ± 0.04	0.99	1.00	
Dithiane-$2I_2$ (16 K)	I_A	-2526 ± 13	0.0	1.47 ± 0.04	1.10	1.34	(7)
	I_B	-1553 ± 13	0.06	0.50 ± 0.04	0.68	0.69	
Pyridine-I_2 in CS_2 (16 K)	I_A	-2631 ± 20	0.10	1.82 ± 0.04	1.15	1.57	(8)
	I_B	-1439 ± 20	0.0	0.39 ± 0.04	0.63	0.62	

a) The e^2Qq values are converted to the ^{127}I nucleus. b) The δ values are relative to the ZnTe source. c) $U_p = -e^2Qq_{\mathrm{obsd}}/e^2Qq_{\mathrm{atom}}$, $e^2Qq_{\mathrm{atom}} = 2292.7$ MHz. d) $\delta = 1.5h_p - 0.54$ (mm s^{-1}).

and bottom (b) spectra of 2AC–3I_2 in Fig. 3 were measured at 16 and 78 K, respectively. These spectra comprise three kinds of quadrupole octets (A, B, and C), as is expected from the crystal structures of 2TPPS–3I_2[3] and 2AC–3I_2[5]. The spectra were fitted with Lorentzian curves of an equal linewidth by a least-squares method using a triple set of the Mössbauer parameters, e^2Qq, η , and δ. The solid curves and the stick diagrams in the figures indicate the best-fitted superimposed Lorentzian curves and the peak positions, respectively. The Mössbauer parameters obtained are summarized in Table 1, together with the results for the usual 1:1 complexes of 1,4-dithiane-iodine[7] and pyridine–iodine.[8] The values of e^2Qq were converted to those for the ^{127}I nucleus.

The Mössbauer spectra of the 2TPPS–3I_2 and 2AC–3I_2 complexes, showing the existence of three unequivalent iodine atoms (I_A, I_B, and I_C), are similar to each other. This observation is in accord with the results of structural analyses for these complexes, in which the iodine groups have a similar configuration. It is established for usual 1:1 molecular complexes that the iodine atom coordinating to the donor atom indicates larger values of e^2Qq and δ than the terminal iodine atom. Therefore, it is appropriate to assign the iodine with the largest quadrupole spltting (A) to the iodine atom (I_A) coordinating to the sulfur or nitrogen atom of each donor molecule, whereas the iodine with the smallest quadrupole splitting (B) should be assigned to the terminal iodine atom (I_B). The intermediate quadrupole splitting (C) corresponds to the iodine molecule (I_C) cross-linked to the two terminal iodine atoms, since the values of e^2Qq and δ are close to those for the solid iodine.[9] The Mössbauer spectrum of 2AC–3I_2 at 78 K is very similar to that previously measured at 85 K by Ichiba et al.[6] It was found from the comparison with the spectrum at 16 K that the absorption peaks corresponding to the intermediate quadrupole splitting (C) decrease more rapidly at 78 K than the other absorption peaks. This result implies that the iodine molecule cross-linked to two I_B atoms has a lower Debye temperature than the other iodine atoms.

The values of e^2Qq, η, and δ are closely related to the charge distribution and the charge density localized on the iodine atom as follows:[10,11]

$$U_p = -e^2Qq_{\text{obsd}}/e^2Qq_{\text{atom}} = -N_z + (N_x+N_y)/2, \tag{1}$$

$$\eta = 3(N_x-N_y)/2U_p, \tag{2}$$

$$\delta = -9.2h_s + 1.5h_p - 0.54, \quad \text{(mm/s, for ZnTe source)}, \tag{3}$$

and

$$h_p = 6-(N_x+N_y+N_z). \tag{4}$$

Here, U_p is the number of unbalanced p-electrons and e^2Qq_{atom}, the atomic iodine quadrupole coupling constant, is equal to 2292.7 MHz for ^{127}I. N_x,N_y, and N_z are the populations of 5p-electrons in the x, y, and z orbitals, respectively. The sign of e^2Qq, obtained directly from the unsymmetrical Mössbauer spectrum, shows whether the main bond of the iodine atom is σ-bonding (z-direction) or π-bonding (x or y direction). The e^2Qq values for all iodine atoms of the present molecular complexes are negative in sign, suggesting that the bonding of each iodine atom is predominantly of the σ-type. The asymmetry parameter (η), the deviation of the electric field from the cylindrical symmetry, is attributed to an additonal π-bonding or an intermolecular bonding in the x or y direction. The large η values for the terminal iodine atoms (I_B) in these complexes are due to the weak intermolecular $I_B \cdots I_C$ bonds, since the bond distances are 3.57 Å and 3.51 Å for 2TPPS–3I_2[3] and 2AC–3I_2[5], respectively (shorter than the sum of the van der Waals radius (4.30 Å)). The isomer shift (δ) is directly related to the s-electron density at the nucleus $|\psi_s(0)|^2$. Since the 5s-electron density is shielded by outer 5p-electrons, the δ value is also dependent on the 5p-electron density. This effect is expressed quantitatively as Eq. 3 by using Slater's shielding coefficients, where h_s and h_p are the numbers of 5s- and 5p-electrons removed from the $5s^25p^6$ (I^-) configuration, respectively. When the bonding of iodine is formed by only $5p_\sigma$-electrons, one expects the relationship $U_p = h_p = 1 \pm i$ to be valid, where i is the ionic character. If $5p_\pi$-electrons take part in bond formation (π-bonding), in addition to $5p_\sigma$-electrons, the relationship $U_p < h_p$ and non-zero η value are generally observed. On the other hand, the contribution of 5s-electrons (sp hybridization) leads to the relationship that $U_p > h_p$ because of the decrease in the s-electron density at the nucleus. The U_p and h_p values obtained for each iodine atom are presented in Table 1 (assuming that there is no contribution of 5s-electrons to the bonding of iodine).

It can be seen for the I_A atom coordinating to the S or N atom of each donor molecule that the h_p value is larger than the U_p value. The same tendency was found in the I_A atoms of the usual 1:1 complexes, such as thioether–iodine[7] and amine–iodine.[6,8] This relation has generally been explained in terms of the presence of double or intermolecular bonding in the x or y direction. However, it is quite difficult for the I_A atom to consider the presence of the double bond or the intermolecular bond from the crystallographic data of 2TPPS–3I_2[3] or 2AC–3I_2.[5] Furthermore, the η value was observed to be zero for the I_A atom in each complex. This phenomenon has been successfully interpreted in terms of the slight contribution of core $4d_\sigma$-electrons (dp hybridization) to the charge-transfer bond formation, in addition to the delocalized three-center four-electron bonding.[7,8] The promotion energy of the $4d_\sigma$-electron is probably compensated for by the stabilization of the charge-transfer bond formation. The contribution of the $4d_\sigma$ hybridization remarkably increases the δ value but hardly increases the e^2Qq value. Therefore, the net charge density is close to that obtained from the e^2Qq value. Consequently, the charge densities localized on the I_A atoms of the 2TPPS–$3I_2$ and 2AC–$3I_2$ complexes were evaluated to be approximately +0.12 e and +0.27 e, respectively, by using Eqs. 4 and 5 in Ref. 8. The same calculations lead to charge densities of +0.07 e and +0.11 e for the I_A atoms in dithiane–iodine[7] and pyridine–iodine[8], respectively.

On the other hand, the relationship $U_p < h_p$ and the non-zero η value for the terminal I_B atom are attributable to the additional intermolecular $I_B \cdots I_C$ bond as previously described. Both I_B atoms of the present complexes were estimated to be negatively charged by about 0.39 e from the h_p values (close to the charge densities on the I_B atoms of the 1 : 1 complexes). From the η values for the I_B atoms, very little charge (ca. 0.06 e for 2TPPS–$3I_2$ and ca. 0.04 e for 2AC–$3I_2$) was found to be transferred to the iodine molecule (I_C) cross-linked to the two I_B atoms along the weak $I_B \cdots I_C$ bond. The charge transfer leads to an increase in the charge densities on the I_C atoms of these complexes. The U_p and h_p values for the I_C atoms are in agreement with each other, indicating that the bonding is mainly due to $5p_\sigma$-electrons. The charge densities localized on the I_C atoms are estimated to be −0.04 e and −0.01 e for the 2TPPS–$3I_2$ and 2AC–$3I_2$ complexes, respectively (from the mean values of U_p and h_p). The charge densities obtained for the I_C atoms agree with those transferred from the I_B atoms within the experimental error. Therefore, the slightly negative charge densities on the I_C atoms are apparently due to the charge transfer from the I_B atoms. This result is consistent with the increase in the bond distance (2.73 Å) between the I_C atoms, compared with the gaseous iodine molecule (2.67 Å), since the transferred charges occupy the antibonding molecular orbital (σ_u^*) of the iodine molecule. The charge densities obtained for the I_A, I_B, and I_C atoms of the investigated complexes from the Mössbauer parameters are presented in Fig. 4, together with those for the 1,4-dithiane–iodine[7] and pyridine–iodine[8] complexes.

As shown in Fig. 4, the I_A atoms in the unusual 2:3 molecular complexes are more positively charged than those in the usual 1 : 1 complexes containing the same donor atoms. This result can be qualitatively interpreted on the basis of the strength of a covalent bond between the donor and the I_A atoms. The positive charge on the donor atom, arising from the charge transfer to the iodine molecule, is delocalized on the I_A atom by back donating along the covalent $S \cdots I_A$ or $N \cdots I_A$ bond. The degree of the back donation increases with an increase in the covalency of the intermolecular bond. It is clear from a comparison of the bond distances that the covalency of the $S \cdots I_A$ bond is stronger in the 2TPPS–$3I_2$ complex than in the 1,4-dithiane–$2I_2$ complex. Therefore, it is concluded that the positive charge density on the I_A atom is dependent on the covalency of the intermolecular

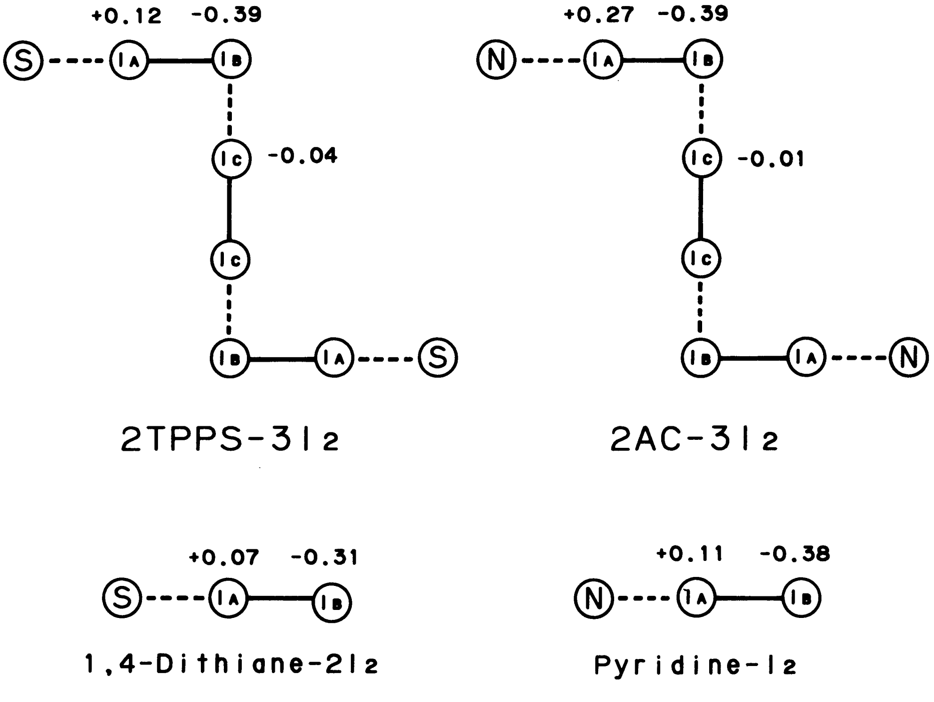

Fig. 4. Charge densities localized on the iodine atoms for the 2TPPS–$3I_2$, 2AC–$3I_2$, 1,4-dithiane–$2I_2$, and pyridine–I_2 complexes.

bond between the donor and the iodine molecules, but not on the degree of the charge transfer from the donor molecule to the iodine molecule. The I_A atoms in the amine complexes are also found to be more positively charged than those in the sulfur-containing donor complexes. As pointed out in our previous paper,⁷⁾ this fact is because the amine cations (N^+), produced by a charge transfer, have a larger electron affinity than the sulfur cations (S^+) in the sulfur-containing donor molecules and, therefore, attract more electrons from the I_A atom than do S^+. The charge densities localized on the I_B atoms in the 2:3 complexes are close to those in the 1:1 complexes, suggesting that the degree of the charge transfer is comparable to each other.

The linear $S \cdots I_A–I_B$ or $N \cdots I_A–I_B$ bond can be essentially described in terms of a delocalized three-center four-electron bonding in the electronic ground state, and resembles the linear triiodide anion (I_3^-) very closely in chemical bonding. The similarity seems to explain the formation of the unusual 2:3 complex: the I_3^- anions combine with the I_2 molecules to form polyiodides such as a pentaiodide anion (I_5^-), a heptaiodide anion (I_7^-), and an octaiodide dianion (I_8^{2-}). The structure of the iodine moieties in the 2TPPS-3I_2 and 2AC-3I_2 complexes is very similar to that of Cs_2I_8, in which the iodine atoms consist of two I_3^- units and one I_2 unit with a flat Z-shaped structure.¹²⁾ Furthermore, the distances of the intra- and intermolecular bonds in the iodine moiety are close to each other.

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References

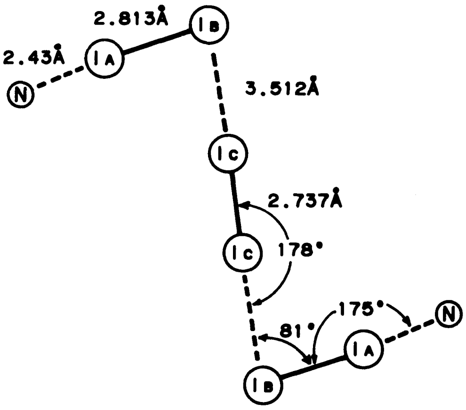
1) R. A. Zingaro and E. A. Meyers, *Inorg. Chem.*, **1**, 771 (1962).

2) G. A. Bowmaker and R. J. Knappstein, *Aust. J. Chem.*, **31**, 2131 (1978).

3) W. W. Schweikert and E. A. Meyers, *J. Phys. Chem.*, **72**, 1561 (1968).

4) G. Y. Chao and J. D. McCullough, *Acta Crystallogr.*, **13**, 727 (1960).

5) T. Uchida, private communication. According to her, the iodine moiety of the 2AC–3I_2 complex is confirmed as follows:



6) S. Ichiba, H. Sakai, H. Negita, and Y. Maeda, *J. Chem. Phys.*, **54**, 1627 (1971).

7) H. Sakai, T. Matsuyama, and Y. Maeda, *Bull. Chem. Soc. Jpn.*, **59**, 981 (1986).

8) H. Sakai, Y. Maeda, S. Ichiba, and H. Negita, *J. Chem. Phys.*, **72**, 6192 (1980).

9) M. Pasternak, A. Simopoulos, and Y. Hazony, *Phys. Rev.*, **140**, 1892 (1965).

10) H. DeWaard, "Mössbauer Effect Data Index 1973," ed by J. G. Stevens and V. E. Stevens, IFI/Plenum Press, New York (1974), P. 447.

11) S. L. Ruby and G. K. Shenoy, "Mössbauer Isomer Shifts," ed by G. K. Shenoy and F. E. Wagner, North-Holland, Amsterdam (1978), Chap. 9b.

12) E. E. Havinga, K. H. Boswijk, and E. H. Wiebenga, *Acta Crystallogr.* **7**, 487 (1954).