Iodine-127 Mössbauer Spectroscopy of Copper(I) Iodide–Phosphine Adducts

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Iodine-127 Mössbauer spectra have been recorded for a variety of CuI–phosphine complexes. None of the spectra obtained showed any resolvable quadrupole splitting and it is concluded that the copper–iodine interaction in these complexes is largely ionic in nature.

Copper(I) iodide forms complexes with a variety of bases, such as amines and phosphines.[1–14] A number of different techniques have been used in attempts to characterize these materials. The most successful of these has been *X*-ray crystallography and a number of different structures have been established for the stoicheiometries CuX·*n*L, where L is an amine, phosphine, or arsine base and X is a halide. A large variety of different structures having this general formulation occur, and the known structural types have been summarized in the literature.[12,15] In these complexes the halogen is found in a number of different environments with one, two, three, or even four close interactions with copper atoms. The CuI–phosphine complexes exhibit Cu–I distances that are approximately equal to or less than the sum of the tetrahedral covalent radii (2.6 Å).[16] The iodine environments in these complexes display lower than cubic symmetry and, if the interactions with copper(I) are covalent, should result in a wide range of ^{127}I quadrupole coupling constants which could be measured by ^{127}I Mössbauer spectroscopy.

We have already established that iodine atoms, in different environments, have quite different quadrupole coupling constants when bonded to elements of the main group. These values can range from *ca.* −3 000 to *ca.* +3 000 MHz depending upon the oxidation state and co-ordination number of the iodine.[17–19] It was therefore our intention to examine, by ^{127}I Mössbauer spectroscopy, a number of CuI–phosphine complexes whose structures were known, in the hope that the Mössbauer parameters would be characteristic of a known geometry type.

The results obtained show that there are no detectable quadrupole splittings for any of the complexes examined. The consequences of this finding are discussed in relation to the nature of the Cu–I bond.

Experimental

The phenylphosphine and triphenylphosphine adducts of copper(I) iodide were prepared according to literature procedures,[4,14] except that tetrahydrofuran was used as solvent in the preparation of $[\{CuI(PPh_3)\}_4]$ instead of chloroform. The melting points were in agreement with the previously reported values. A sample of $[\{(CuI)_2(S_2Et_2)\}_n]$[11] was provided by Professor P. M. Boorman, University of Calgary.

Mössbauer Spectroscopy.—The technical details involved in obtaining the ^{127}I Mössbauer spectra have been fully described elsewhere.[17] The spectra were computer fitted using a program which incorporates full transmission-integral procedures.[20] In all cases the source linewidth was arbitrarily fixed at the natural value of 1.27 mm s^{-1}. Since all the spectra appeared as single lines with no resolvable splitting, the ^{127}I Mössbauer parameters, displayed in the Table, correspond to fits of the data with a single line, thickness broadened, but with no quadrupolar coupling. To estimate the maximum possible values of the unresolved quadrupolar couplings several of the spectra were fitted by an alternative method in which the absorber linewidth was fixed, and the value of eQV_{zz} which gave the best agreement with the experimental data was determined. The signs of the eQV_{zz} parameters were assigned on the basis of point-charge calculations of V_{zz} for the known geometries about iodine in these complexes. The asymmetry parameter, η, was fixed at 0.0 for these computations although, for some of the sites considered, this condition is not expected. Allowing η to vary during the iterative fitting procedure resulted in non-convergence or in unrealistic values.

Results and Discussion

The ^{127}I Mössbauer data that we have obtained for a number of CuI complexes are summarized in the Table. Representative spectra are shown in the Figure. The single striking feature of these spectra is that none of them displays any resolvable quadrupole coupling. In fact the half-height linewidths of these spectra, obtained by assuming $eQV_{zz} = 0$ in one fitting procedure, are comparable to that found for CuI, in which the tetrahedrally co-ordinated iodine atoms should experience negligible electric field gradients and hence negligible quadrupole coupling. We have noted that the linewidth of the resonance for CuI can be reduced to about 2 mm s^{-1} by considerably reducing the sample size.[21] Even if thickness broadening is minimized, it is nevertheless apparent that the quadrupole couplings of the iodine nuclei in the adducts are too small to be resolved by ^{127}I Mössbauer spectroscopy. The variations in linewidths for the different samples are to a large extent a consequence of different absorber thicknesses and the high degree of correlation between the absorber linewidth and the dimensionless thickness parameter in the simulations.

The maximum possible magnitudes of the coupling constants ($e^{127}Q_gV_{zz}$) in these adducts are indicated in the Table. By comparison, genuinely covalent interactions of iodine bonded to main-group elements, in non-cubic configurations, can give rise to quadrupole coupling constants as large as 3 000 MHz.[17–19] There have been relatively few iodine Mössbauer investigations of iodide bonded to transition metals, however, a number of ^{129}I Mössbauer results have been reported for the iodo-ligand in platinum(II) co-ordination compounds.[22] Conversion of the ^{129}I quadrupole coupling constants for these species, which contain iodine terminally bonded to platinum, into the corresponding values for ^{127}I yields values ranging from 770 to 1 190 MHz. The maximum possible values, reported herein, for the CuI·*n*PPh$_3$ complexes are significantly smaller, as expected,[22] on the basis of the hard and soft acid and base theory.

A recent report of a copper(I)–iodine complex anion $[CuI_3]^{2-}$ describes the iodine quadrupole coupling constants which were determined by n.q.r. spectroscopy.[23] The $|e^{127}Q_gV_{zz}|$ values were found to be of the order of 350 MHz which is indeed below the limit of resolution of the ^{127}I Mössbauer experiment. Those authors estimated that the Cu–I bonds in $[CuI_3]^{2-}$ have an ionic character of 0.85. Our

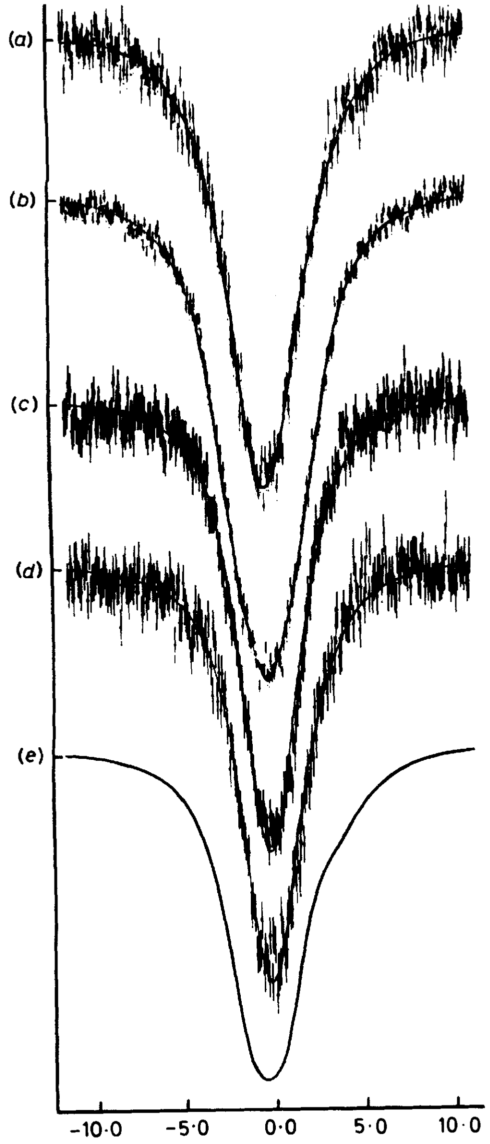

Figure. ^{127}I Mössbauer spectra of some copper(I) iodide complexes: (*a*) CuI, (*b*) [{CuI(PPh$_3$)}$_4$], (*c*) [(CuI)$_2$(PPh$_3$)$_3$], (*d*) [CuI(PPh$_3$)$_3$], and (*e*) simulated spectrum with $e^{127}Q_gV_{zz}$ = 800 MHz

Table. ^{127}I Mössbauer parameters for complexes of CuI assuming (*i*) single lines, (*ii*) quadrupole-split sites

Complex		Isomer shift[a]/ mm s^{-1}	$e^{127}Q_gV_{zz}$[b]/ MHz	Γ_{abs}[c]/ mm s^{-1}
[CuI(PPh$_3$)$_3$]	(*i*)	−0.12(6)		2.64(24)
	(*ii*)	−0.03(6)	−470(60)	1.7[d]
[(CuI)$_2$(PPh$_3$)$_3$]	(*i*)	−0.10(6)		2.61(21)
	(*ii*)	−0.04(6)	−450(50)	1.7[d]
[{CuI(PPh$_3$)}$_4$]	(*i*)	−0.12(3)		3.83(12)
	(*ii*)[e]	−0.65(9)	−620(70)	1.7[d]
		+0.42(12)	690(60)	1.7[d]
[{CuI(PH$_2$Ph)$_2$}$_2$]	(*i*)	−0.06(6)		2.56(18)
	(*ii*)	+0.01(6)	−410(60)	1.7[d]
[{(CuI)$_2$(S$_2$Ph$_2$)}$_n$]		−0.09(3)		3.45(9)
CuI		−0.03(6)		3.77(3)

[a] Relative to that of K^{127}I. [b] Signs assigned (not determined). [c] Γ_{source} arbitrarily assigned the natural linewidth of 1.27 mm s^{-1}. [d] Assigned value. [e] Two sites fitted on the basis of the known structure.

Mössbauer results indicate that the various neutral complexes studied have comparable ionic character in their Cu–I bonds.

It must, therefore, be concluded that for the copper(I)–iodine complexes there is very little distortion of the electronic environment of iodine from the spherical valence configuration of the purely ionic iodide ion. This would seem to indicate that the nature of the 'bond' between iodine and copper is not covalent. Alternatively this could imply that, in the bonding, electrons are withdrawn nearly equally from all of the valence *p* orbitals of iodine. This is conceivable for triply or quadruply bridging iodine environments, but not for dibridging or terminal environments. The possibility that a lattice contribution to the electric field gradient cancels the valence contribution seems rather unlikely in view of the wide range of iodine environments. Consequently it seems reasonable to conclude that in the compounds studied, and probably in most Cu–X complexes where X is a halogen, the Cu–X interactions are primarily electrostatic attractions of the copper(I) and halide ions, perhaps somewhat analogous to hydrogen bonding. This is reflected in the observation that the bonding to either copper(I) or halide ions in such complexes shows little directional preference. Similarly, the Cu–X distance is relatively insensitive to the nature of the other substituents on the copper(I) ion and depends primarily on the co-ordination number.[15]

We hope to investigate other transition metal–iodine complexes in which iodine quadrupolar coupling may be of larger magnitude than those reported here. In the Pt–I complexes studied by in ref. 22 the quadrupole coupling constants at iodine were of such magnitudes as to be clearly resolvable using the ^{127}I isotope (see Figure), although still indicative of largely ionic interactions. It might be expected that the largest possible quadrupole coupling for iodine in a copper(I) complex would occur for a terminal iodide ligand bonded to a copper atom of the lowest possible co-ordination number.

Acknowledgements

The Natural Sciences and Engineering Research Council of Canada are thanked for financial support and for scholarships (to R. J. B.).

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Received 25*th October* 1984; *Paper* 4/1830