crowding in the plane of the Ir complex brought about by the trimethylene chelate links in the dpp ligands, thus leading to a weaker P–Ir interaction. On the other hand the higher CO bond order in the vpa complex indicates that vpa has a greater tendency than dpe to delocalize electrons from iridium, and this may be due to the better overlap between the π orbitals on the As and Ir atoms or be due to the presence of the double bond in the vpa chelate backbone. In fact the latter factor is probably more important as ν(CO) appears at 1955 cm^{-1} in the infrared spectrum of $[Ir(CO)(vpp)_2]Cl$.[5]

Both $[Ir(L\frown L)_2]Cl$ compounds ($L\frown L$ = dpp, vpa) form stable, irreversible oxygen adducts, $[Ir(L\frown L)(O_2)]Cl$, which exhibit $\nu(O_2)$ bands at 830 cm^{-1} (dpp) and 840 cm^{-1} (vpa).

This work has shown that using ligands of type $Ph_2L\frown L'Ph_2$ (L, L′ = P, As) in reactions with *trans*-$Ir(CO)Cl(PPh_3)_2$ does not produce stable products when L = L′ = As and that the type of backbone in the chelate is very important, for in the system L = P, L′ = As reaction occurs with ligand containing the *cis*-CH=CH– linkage but not with the $-CH_2CH_2-$ linkage. Moreover, even with diphosphine ligands, the chelate backbone exerts a profound effect since the dpc ligand does not react with $Ir(CO)Cl(PPh_3)_2$. It can also be seen that when reaction does occur, the chelate backbone exerts a large influence on the resulting complex as illustrated by the large difference in ν(CO) in the dpe and dpp complexes.

Registry No. $Ir(CO)Cl(PPh_3)_2$, 15318-31-7; $[Ir(CO)(L\frown L)_2]Cl$; $L\frown L$ = dpp, 39494-90-1; $[Ir(CO)(L\frown L)_2]Cl$; $L\frown L$ = vpp, 36390-33-7; $[Ir(CO)(L\frown L)_2]Cl$; $L\frown L$ = vpa, 39494-85-4; $[Ir(L\frown L)_2(O_2)]Cl$; $L\frown L$ = dpp, 39494-86-5; $[Ir(L\frown L)_2(O_2)]Cl$; $L\frown L$ = vpa, 39494-87-6; $[Ir(dpp)_2]Cl$, 39494-88-7; $[Ir(vpa)_2]Cl$, 39494-89-8.

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X-Ray Photoelectron Spectra of Ethylenediaminetetraacetic Acid and Its Metal Complexes[1]

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The protonation of polyaminocarboxylic acids in solution and in the solid state has been reported in the literature. The complexes formed between the ions of the alkaline earths and ethylenediaminetetraacetic acid (EDTA) have been studied extensively in terms of their properties in solution.[3] Although the ability of EDTA to form stable complexes in solution with many polyvalent metal ions is firmly established, little is known of the properties and structures of these complexes in the solid state. EDTA complexes have been studied by infrared spectroscopy offering some information about metal-carbonyl bonding, but there is still disagreement regarding the nature of bonding.[4]

Table I. Binding Energies from Photoelectron Spectra[a] of H_4EDTA and Its Salts[b]

Compd	E_B(N 1s), eV	Compd	E_B(N 1s), eV
H_4EDTA	402.2	Mg_2EDTA	399.8
Na_2H_2EDTA	402.6	$CaNa_2EDTA$	400.1
Na_4EDTA	400.3	$CuNa_2EDTA$	400.1
MgH_2EDTA	399.8, 402.2	$ZnNa_2EDTA$	400.3

[a] Obtained from spectra using Mg Kα X-rays. [b] Average binding energies for C 1s: 286.0, 288.5 eV. Average binding energy for O 1s: 531.5 eV.

In this paper we present data from X-ray photoelectron spectroscopy. From such data one may learn about the electrostatic environment surrounding each atom in the molecule.[5] Photoelectron spectra were obtained on EDTA tetraacid, disodium dihydrogen EDTA, dimagnesium EDTA, magnesium dihydrogen EDTA, calcium disodium EDTA, copper disodium EDTA, and zinc disodium EDTA.

Experimental Section

Photoelectron spectra were taken with a double-focusing electrostatic electron spectrometer, located in the Physics Division of the Oak Ridge National Laboratory. Details of this spectrometer have been presented elsewhere.[6] Magnesium Kα X-rays (1254 eV) were used as a photon source. The data were taken with 0.1% resolution.

Binding energies were derived from the photoelectron data by means of the familiar relationship $E_B = h\nu - E_e$, where E_B is the binding energy, $h\nu$ is the photon energy, and E_e is the measured photoelectron energy. The binding energies have been standardized to gold evaporated onto the surface. The Au 4f binding energy is taken as 83.8 eV. Supplementary calibration was obtained by mixing KCl with the samples and using the K $2p_{3/2}$ level as a standard (295.0 eV).

The preparations of the various solids studied in this paper were made with slight modifications based on previous procedures.[4c]

Zinc EDTA, disodium EDTA, and dimagnesium EDTA were obtained from J. T. Baker Chemical Co. Except for zinc EDTA, they were recrystallized.

Ethylenediaminetetraacetic acid, magnesium salt ($H_2MgEDTA$), was precipitated by mixing magnesium sulfate solution and H_2Na_2-EDTA solution at pH 4.5. The crystals obtained after several days were washed with acetone and dried in a vacuum desiccator.

Results and Discussion

The photoelectron spectra in the region of the K-shell binding energy for carbon and oxygen remained fairly constant throughout the series of compounds. The carbon spectra showed two principal peaks corresponding to the average binding energies of 286.0 and 288.5 eV, while a single binding energy was determined for oxygen of 531.5 eV. The deviation among the different samples for carbon and oxygen was not larger than several tenths of 1 eV. The most interesting results were obtained on the 1s binding energies of nitrogen, which fell into one of two groups depending on the nature of the EDTA compound (*cf.* Table I

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(1) This research jointly sponsored by the University of Missouri, University of Tennessee, and the U. S. Atomic Energy Commission under contract with Union Carbide Corp.

(2) (a) University of Missouri–Kansas City. (b) Student guest assignee at ORNL from the University of Tennessee supported by a National Science Foundation Grant. (c) Address all correspondence to this author at the Physics Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830.

(3) E. Lin, A. A. Sandoval, and K. L. Cheng, *J. Magn. Resonance*, 4, 301 (1971).

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(5) K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johansson, T. Bergmark, S. E. Karlsson, I. Lindgren, and B. J. Lindberg, *Nova Acta Regiae Soc. Sci. Upsal.*, **20**, (1967).

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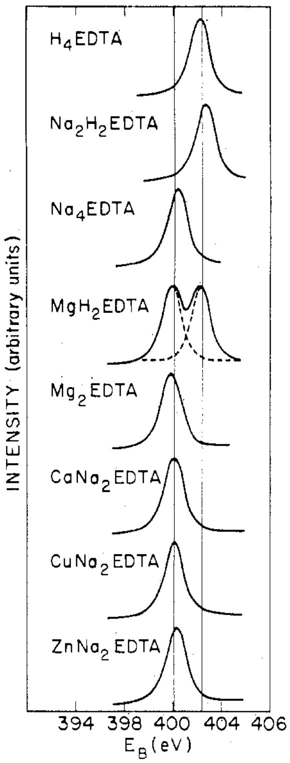
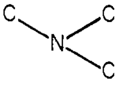


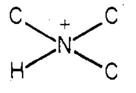
Figure 1. Photoelectron spectra in region of N 1s binding energy for various EDTA compounds. E_B is binding energy obtained using Mg Kα X-rays (1254 eV). Solid vertical lines indicate average energies for the two groups of nitrogen binding energies.

and Figure 1). (The relative binding energies have a standard deviation of ±0.2 eV although the absolute values are known with less certainty.) Photoelectron spectra of sodium and the other cations were also determined and they confirmed the elemental composition of the solid.

As has been thoroughly demonstrated,[5] the inner-shell binding energies will shift according to changes in the electrostatic environment, higher binding energies occurring with a higher positive atomic charge. Siegbahn, *et al.*,[5] have also correlated binding energies for nitrogen with a calculated charge based on Pauling's scale of electronegativity. In EDTA compounds there would appear to be two possible environments for nitrogen, the unprotonated form



and a protonated form



These two forms yield calculated charges, q_p, of respectively −0.18 and +0.25 which from Figure V:34 of ref 5 give the respective binding energies 398.4 and 400.7 eV. These values are slightly lower than the average value of the two groups found in this work, but the energy separation of 2.3 eV is in good agreement. Thus one sees from the photoelectron data that H_4EDTA and NaH_2EDTA can be correlated with the protonated form of nitrogen, while Na_4EDTA, Mg_2EDTA, $CaNa_2EDTA$, $CuNa_2EDTA$, and $ZnNa_2EDTA$ possess only the unprotonated forms. MgH_2EDTA appears to have nitrogen with two different binding energies—one is apparently protonated while the other is unprotonated.

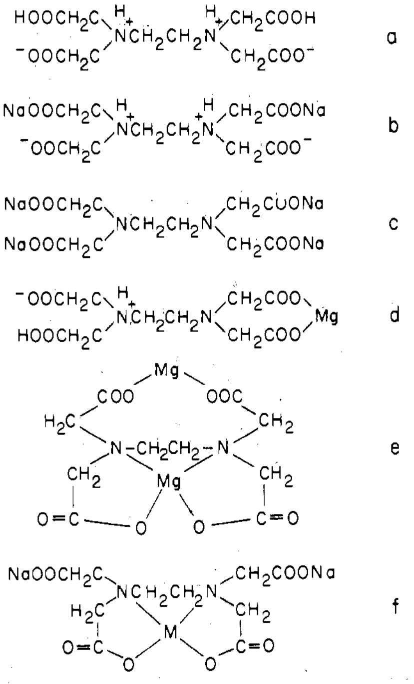


Figure 2. Structures suggested for various compounds of EDTA: (a) H_4EDTA, (b) Na_2H_2EDTA, (c) Na_4EDTA, (d) MgH_2EDTA, (e) Mg_2EDTA, and (f) MNa_2EDTA where M is Ca, Cu, or Zn.

Based on our interpretation of the photoelectron spectra as to whether the nitrogens were protonated or not, we have given in Figure 2 possible structures for EDTA and its salts. Structures a and b (Figure 2) are supported by X-ray diffraction[4a,7] which has indicated the zwitterion structure of EDTA. O'Donnell[8] has studied crystals of MgH_2EDTA formed at pH 3.0 and concluded that Mg is not complexed, in agreement with structure d, but that both nitrogens are protonated, which is in disagreement with our data. Divalent metals should be complexed[9] for the remainder of the EDTA salts as shown by structures e and f. Structure e suggests that magnesium should exist in two chemical environments. However, we found in our photoelectron spectrum for magnesium only one peak. From analysis of the data, we can say that if two forms of Mg exist, the core binding energies corresponding to the two species must differ by less than 0.3 eV. This may not be unreasonable, since it is known that chemical shifts in the core electrons of magnesium compounds are generally rather small.[10]

Radiation Damage

It is noted in the studies on H_4EDTA, Na_2H_2EDTA, and MgH_2EDTA that with continuous radiation an extra nitrogen peak grew which exhibited a binding energy about 2 V lower than that assigned to the protonated nitrogen. This behavior was studied in detail for H_4EDTA, and it was found that the growth of the new photoelectron peak was exponential with the time of radiation rising to an asymptotic value after several hours, at which time two different nitrogen peaks were observed with equal intensity. These binding energies corresponded to the chemical environment of a protonated and unprotonated nitrogen. A similar observation was made on the photoelectron spectrum of a related compound, *N*-(2-

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(9) For example, see A. E. Martell and M. Calvin, "Chemistry of Metal Chelate Compounds," Prentice-Hall, New York, N. Y., 1952 p 15.

(10) W. E. Moddeman and R. G. Albridge, private communication.

hydroxyethyl)ethylenediaminetriacetic acid. No other changes in the spectra of any of the other compounds were observed as the result of radiation damage. The data reported in this paper are for spectra extrapolated back to zero irradiation time.

Registry No. H$_4$EDTA, 60-00-4; Na$_2$H$_2$EDTA, 139-33-3; Na$_4$EDTA, 64-02-8; MgH$_2$EDTA, 3459-31-2; Mg$_2$EDTA, 39208-13-4; CaNa$_2$EDTA, 39208-14-5; CuNa$_2$EDTA, 39208-15-6; ZnNa$_2$EDTA, 39208-16-7.

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Contribution from the Chemistry Department,
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Mechanistic Studies of Chemical-Exchange Reactions by Complete Nuclear Magnetic Resonance Line Shape Fitting. III. Ten-Site Halogen Exchange in Binary Mixtures of Trimethyltin Halides

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Halogen exchange in binary mixtures of SnCl$_4$, SnBr$_4$, and SnI$_4$ were first investigated by Burke and Lauterbur[1] using nuclear magnetic resonance. Mixed halides were found to form in a moderately rapid reaction and ^{119}Sn magnetic resonance signals could be identified for all mixed halides SnX$_n$Y$_{4-n}$. The equilibria, as far as could be determined, represented a random redistribution of halogen atoms among the tin compounds. Nonrandom redistribution of halogen atoms and alkyl groups was also studied independently by Grant, *et al.*,[2] and Van den Berghe, *et al.*,[3] under both equilibrium and nonequilibrium conditions in reactions of R$_n$SnX$_{4-n}$ compounds.

A recent study using proton magnetic resonance by Van den Berghe, *et al.*,[4] of binary mixtures of methyltin halides showed that halogen exchange could be rapid or slow on the nmr time scale and was dependent on the particular mixed halide and on the solvent in some cases. No mention of the dependence of exchange on the concentration of the components, the effect of impurities, or the mechanism of the reaction was made.

A preliminary study with emphasis on purity of reactants and solvents was made of halogen exchange in binary mixtures of dimethyltin dihalide,[5] and a simple mechanism was proposed for the process. With the utilization of a generalized method[6] to study the mechanism of a chemical-exchange reaction using pseudo-first-order rate constants in a complete nmr line shape fitting, the fifteen-site[7] halogen exchange in binary mixtures of dimethyltin dihalides was much simplified and studied in detail.[8] This note reports a similar study on trimethyltin halides and comparison will be drawn where appropriate between the two systems.

In the fast-exchange region the proton magnetic resonance spectrum of a binary mixture of trimethyltin halides consists of five peaks, one intense main peak in the middle and two satellites on each side. Because of the similar magnetogyric ratios of ^{117}Sn and ^{119}Sn, their satellites are only about 1 Hz apart. If the exchange is slowed down by either lowering the temperature of the system or addition of an appropriate retarding agent, the complete spectrum in the slow-exchange limit consists of ten peaks, two main peaks corresponding to the two constituents and their eight satellites. If the ^{117}Sn and ^{119}Sn satellites remain well resolved in the fast-exchange limit for the halogens, then there is a negligible rate of breaking and forming of Sn–C bonds in the system at least at around room temperature or below. Thus the spin-spin coupling is preserved during the exchange process and the ten-site problem can be simplified to a mere two-site problem,[5,6,8] which is repeated with appropriate intensity adjustments five times.

Experimental Section

Purification of Trimethyltin Chloride and Trimethyltin Bromide. Trimethyltin chloride and trimethyltin bromide were obtained commercially from Alfa Inorganics, Inc. The chloride was purified by recrystallization from carbon tetrachloride and dried in a desiccator under reduced pressure. The bromide was first distilled *in vacuo* at room temperature and then recrystallized from carbon tetrachloride in an ice bath as the bromide has a melting point around room temperature.

Preparation of Trimethyltin Iodide. Trimethyltin iodide was prepared from trimethyltin hydroxide and hydriodic acid. The crude iodide resulted from the reaction

$$(CH_3)_3SnOH + HI \rightarrow (CH_3)_3SnI + H_2O$$

in aqueous medium which was colored reddish brown by the iodine usually present due to slight decomposition of the rather unstable iodide. The solution was decolorized by treatment with sodium thiosulfate and was then shaken with several portions of chloroform to extract the trimethyltin iodide. The chloroform was removed from the extract by evaporation under reduced pressure. The viscous liquid was then distilled *in vacuo* at room temperature and the distillate was finally recrystallized at a subzero temperature from toluene in a Dry Ice–acetone bath. The trimethyltin iodide is a colorless liquid when freshly prepared but turns slightly yellowish in 4 or 5 days even when kept in a refrigerator in the dark.

Preparation of Nmr Samples and Their Storage. Binary mixtures of the three trimethyltin halides were prepared with about 1% by weight of TMS in toluene of Spectro Quality previously and permanently dried by keeping over molecular sieve. Standard 5-mm o.d. nmr tubes were used. In the upper part of each tube a glass wool plug was inserted and some molecular sieve (Linde 4A) was suspended above it. After that the samples were degassed by the conventional freeze–pump–thaw cycles and then sealed. The spectra were recorded within 3 days (at the most) and while not in use were always stored in the dark in a refrigerator. The above precautions were made to reduce to a minimum the presence of water or other hydroxylic impurities to which the chemical-exchange rates of the halogens in

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[6] S. O. Chan and L. W. Reeves, *J. Amer. Chem. Soc.*, **95**, 670 (1973).

[7] In a binary mixture of dihalides, formation of the mixed halide results in three main species. Naturally occurring tin has two magnetic isotopes with spin $^1/_2$ properties and appreciable abundances, namely, 7.67% ^{117}Sn and 8.68% ^{119}Sn. Coupling of the methyl proton to these magnetic tin nuclei gives rise to two satellites on each side of a main peak amounting altogether to 15 peaks in a resolved spectrum.

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