A mixed-metal complex, $[Co(Smc)_2Ag]NO_3 \cdot H_2O$, was obtained by treating $[Co(Smc)_2]$ with silver nitrate in water. The visible spectrum of the $[Co(Smc)_2Ag]NO_3 \cdot H_2O$ complex differs very little from that of $[Cd(Smc)_2]$, suggesting that in the former the coordination about the Co(II) atom is still $[CoN_2O_4]$. The appearance of a weak absorption in the infrared spectrum of $[Co(Smc)_2Ag]NO_3 \cdot H_2O$ at 380 cm^{-1}, assigned to ν(Ag-S),[6] is evidence of the formation of bonds between the originally uncoordinated thioethers and silver ion.

It should also be mentioned that no complex of the type $Li[Ag(Smc)_2]$ could be prepared. Numerous attempts were made to isolate such a derivative, both in daylight and in the dark. This contrasts sharply with the ready availability of $Li[AgMt_2]$.[7]

A closer examination of the results obtained from this work and previous work on DL-methionine[7,12] and *S*-methylcysteine[6] complexes indicates that there are, as expected and as has already been realized, similarities between the donor properties of these two ligands. However, the present work has shown some significant differences. The similarities and differences can be summarized as follows. Similarities: (a) isostructural $[ML_2]_n$ complexes (M = Co, Ni, Cu, Zn; L = Mt, Smc) containing the $[MN_2O_4]$ donor set; (b) the existence of similar mixed-metal complexes. Differences: (a) the existence of complexes $[ML_3]^-$ (when L = Mt, for Ni but not for Cu; when L = Smc, for Cu but not for Ni); (b) exactly similar reaction conditions produce $[Pd(MtH)Cl_2]$ and $[Pd_2(SmcH)_2Cl_2][PdCl_4]$; (c) the existence in the solid state of $Li[AgMt_2]$ but not of $Li[Ag(Smc)_2]$.

Registry No. $[Cu(Smc)(NO_3)]$, 39532-20-2; $Na[Cu(Smc)_3]$, 39494-99-0; $Pd_3(SmcH)_2Cl_6$, 39495-00-6; $[Co(Smc)_2Ag]NO_3 \cdot H_2O$, 37339-69-8.

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Reaction between *trans*-Carbonylchlorobis(triphenylphosphine)iridium and Some Bidentate Group Vb Chelates

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Received November 17, 1972

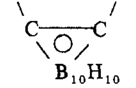
Since Vaska showed that *trans*-$Ir(CO)Cl(PPh_3)_2$ reversibly binds oxygen,[1] interest in synthetic oxygen carriers has grown rapidly. Work published recently has examined differing aspects of these systems: the O-O distance in the complexes,[2] oxygen uptake as a function of ligand,[3] and the effect of differing d^8 metal ions.[4] As part of a program aimed at studying synthetic oxygen carriers involving multidentate ligands, which may relate to natural oxygen transporters, we have begun, and wish to report here on, the reaction of a series of bidentate group Vb ligands with Vaska's compound.

Table I. Analytical and Infrared Data of the Complexes

	% carbon		% hydrogen		Ir spectra, cm^{-1}	
	Calcd	Found	Calcd	Found	ν(CO)	$\nu(O_2)$
$[Ir(CO)(dpp)_2]Cl$	61.1	61.0	4.8	4.6	1910	
$[Ir(dpp)_2]Cl$	61.5	61.3	4.9	4.7		
$[Ir(dpp)_2(O_2)]Cl$	59.6	59.7	4.8	4.8		830
$[Ir(CO)(vpa)_2]Cl$	55.9	56.0	3.9	3.6	1950	
$[Ir(vpa)_2]Cl$	56.3	56.5	3.9	3.9		
$[Ir(vpa)_2(O_2)]Cl$	54.6	54.8	3.9	3.7		840

The ligands employed in this study were 1,3-bis(diphenylphosphino)propane (dpp), 1,2-bis(diphenylarsino)ethane (dae), *cis*-1,2-bis(diphenylarsino)ethylene (vaa), *cis*-1-diphenylphosphino(2-diphenylarsino)ethylene (vpa), 1-diphenylphosphino(2-diphenylarsino)ethane (pae), and bis(diphenylphosphino)-*o*-carborane (dpc). We also used *cis*-

dpc =



1,2-bis(diphenylphosphino)ethylene (vpp), but while our work was in progress, Doronzo and Bianco published the results of a similar study.[5] Our results are in agreement with theirs.

Experimental Section

The Ligands. These were prepared by literature methods[6] or by methods to be published shortly.[7]

The Complexes. The method used in complex synthesis was similar to that of Vaska and Catone[8] and involved the steps

$$Ir(CO)Cl(PPh_3)_2 \xrightarrow[C_6H_6,\ \text{cold}]{L\frown L} [Ir(CO)(L\frown L)_2]Cl \xrightarrow[\text{toluene, 1-propanol}]{\text{reflux}}$$

$$[Ir(L\frown L)_2]Cl \xrightarrow[C_6H_6]{O_2} [Ir(L\frown L)_2(O_2)]Cl$$

Analyses were determined by the Microanalytical Laboratory of this department (see Table I). Infrared spectra were obtained as Nujol or hexachlorobutadiene mulls on a Perkin-Elmer 621 spectrophotometer.

Results and Discussion

With the ligands dae, vaa, pae, and dpc no reaction occurred upon mixing with Vaska's compound in benzene; even after reflux both the ligand and $Ir(CO)Cl(PPh_3)_2$ appeared to be unchanged. However, reaction did occur with the ligands dpp, vpp, and vpa. In the infrared spectra of the $[Ir(CO)(L\frown L)_2]Cl$ complexes ν(CO) bands were observed at 1910 cm^{-1} (dpp) and 1950 cm^{-1} (vpa). These frequencies may be compared with that of the analogous complex $[Ir(CO)(dpe)_2]Cl$ (dpe = 1,2-bis(diphenylphosphino)ethane), which exhibits ν(CO) at 1933 cm^{-1}.[8] Although there is some risk involved in speculating the extent of back-bonding in complexes which have not been proved to be isostructural, it may nonetheless be mentioned that the low frequency of the dpp adduct compared with that of dpe may indicate a lower CO bond order in the dpp complex because of decreased back-donation from the metal to the phosphine. This rather surprising result may be explained as due to the increased steric

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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.

Acknowledgments. K. K. C. is grateful to The British Council for a Fees Award, and S. G. M. thanks the Science Research Council for a Research Studentship.

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

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Received November 20, 1972

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	$CaNa_2$EDTA	400.1
Na_4EDTA	400.3	$CuNa_2$EDTA	400.1
MgH_2EDTA	399.8, 402.2	$ZnNa_2$EDTA	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

(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.

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