known isomers of the triethylenetetramine complex Co(trien)OX$^+$.[4] To demonstrate the correctness of our assignments of configuration, we have followed the procedure of Buckingham, Marzilli, and Sargeson,[5] converting each optically active oxalatotetramine complex into the corresponding *trans*-dichlorotetramine derivative. The preference of the tetramines 2,3,2-tet and 3,2,3-tet for the *trans* configuration facilitates this transformation in the acidic medium required for retention of configuration at the coordinated secondary amine nitrogen atoms. We have assigned the absolute configurations to the *trans*-dichlorotetramine complexes by comparing their ORD and CD curves with those of the known triethylenetetramine complexes. The configurations of this family of complexes are related by the scheme

$$\underset{[\mathrm{M}]_{\mathrm{D}} = +880°}{\Lambda\text{-}\beta\text{-}(SS)\text{-}[\mathrm{Co(trien)Cl_2}]\mathrm{ClO_4}} \underset{\text{reflux 30 min}}{\overset{\mathrm{BH_3OH{-}HCl}}{\rightleftarrows}} \underset{[\mathrm{M}]_{\mathrm{D}} = +3000°}{\textit{trans}\text{-}(SS)\text{-}[\mathrm{Co(trien)Cl_2}]\mathrm{ClO_4}}$$

$$\underset{[\mathrm{M}]_{503} = +5050°}{\Lambda\text{-}\beta\text{-}(RR)\text{-}[\mathrm{Co(2,3,2\text{-}tet)OX}]\mathrm{ClO_4}} \underset{\mathrm{H_2C_2O_4}}{\overset{\mathrm{HCl}}{\rightleftarrows}} \underset{[\mathrm{M}]_{\mathrm{D}} = -880°}{\textit{trans}\text{-}(RR)\text{-}[\mathrm{Co(2,3,2\text{-}tet)Cl_2}]\mathrm{ClO_4}}$$

$$\underset{[\mathrm{M}]_{521} = -5000°}{\Lambda\text{-}\alpha\text{-}(RR)\text{-}[\mathrm{Co(3,2,3\text{-}tet)OX}]\mathrm{ClO_4}} \underset{\mathrm{H_2C_2O_4}}{\overset{\mathrm{HCl}}{\rightleftarrows}} \underset{[\mathrm{M}]_{\mathrm{D}} = +390°}{\textit{trans}\text{-}(RR)\text{-}[\mathrm{Co(3,2,3\text{-}tet)Cl_2}]\mathrm{ClO_4}}$$

It has been shown that the configuration of the coordinated secondary nitrogen atoms control the course of the interconversion of *trans*-Co(trien)Cl$_2^+$ and β-*cis*-Co(trien)Cl$_2^+$, which involves the shift of one donor atom.[5] The interconversion of *trans*-Co(3,2,3-tet)Cl$_2^+$ and α-*cis*-Co(3,2,3-tet)OX$^+$ is the only example known to us in which the configuration of the secondary amine groups controls the stereochemistry of the shift of *two* donor atoms. In contrast with the chemistry of cobalt(III) complexes with triethylenetetramine, we find that the oxalato and dichloro 2,3,2-tet and 3,2,3-tet complexes are completely interconvertible within each series—oxalato to dichloro in excess hydrochloric acid and dichloro to oxalato in excess oxalic acid. In each case, interconversion proceeds to give a single product with more than 90% retention of configuration.

These reactions not only demonstrate the power of dissymmetric donor atoms to control the steric course of isomerization within the coordination sphere of a metal ion but also suggest that reaction pathways in which more than one donor atom is shifted are more readily accessible than has been supposed.

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Photoelectron Spectroscopy of Coordination Compounds. Triphenylphosphine and Its Complexes

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In the past few years photoelectron spectroscopy has been refined to the point where it can now be used to relate the chemical environment of an atom and the electron density about that atom by means of an absolute determination of electron-binding energies.[1] We wish to report the results of a study utilizing this method on some coordination compounds where back-donation may be important.

The use of photoelectron spectra to determine the effect of coordination on the electron density of a ligand is based on the fact that changes in the electron density about an atom are reflected in changes in the binding energies of the core electrons. Larger binding energies are associated with smaller electron densities.[1,2] Since coordination by simple electron pair sharing is always expected to lead to a decrease in the electron density of the ligand, one can anticipate that it should lead to larger values for the binding energies of the core electrons of the literal donor atom of the ligand. This effect will be altered where π bonding is also involved. Where π bonding involves back-donation from filled metal ion orbitals to empty ligand orbitals, the effect of π bonding is expected to counter the effect of σ bonding. In addition, in a series of compounds, there will be effects that are related to the electronegativity differences between the coordinated atoms.

In order to examine the use of photoelectron spectra in estimating the relative importance of these factors we have used such spectra to obtain the binding energies of the phosphorus 2p electrons in the compounds $(C_6H_5)_3P$, $(C_6H_5)_3P{=}O$, $Ni(P(C_6H_5)_3)_2Cl_2$, $Pd(P(C_6H_5)_3)_2Cl_2$, and $Cd\,(P\,(C_6H_5)_3)_2Cl_2$.

Experimental Section

The spectra were obtained by means of a 35-cm double-focusing electron spectrometer of the split-coil solenoidal type.[3] The majority of runs were taken at an instrumental momentum resolution of 0.05%. The spectra were calibrated using the carbon 1s line of triphenylphosphine as an internal standard. The C_{1s} binding energies and $\beta\rho$ values corresponding to the anodes used are listed in Table I.

All analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. The nickel complex was prepared by the method of Cotton, Faut, and Goodgame.[4] A similar procedure

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TABLE I

ELECTRON-BINDING ENERGIES IN $(C_6H_5)_3P$ AND SOME OF ITS COMPLEXES

Compound	Binding energies,[a] eV		
	P_{2p}	Cl_{2p}	M
$(C_6H_5)_3P$	131.9 ± 0.4 (7 runs)		
$(C_6H_5)_3P{=}O$	132.9 ± 0.1 (4 runs)		
$Ni(P(C_6H_5)_3)_2Cl_2$	131.6 ± 0.3 (5 runs)	199.1 ± 0.2 (4 runs)	855.2 ± 0.8[b] (5 runs)
$Pd(P(C_6H_5)_3)_3Cl_2$	131.7 ± 0.1 (5 runs)	198.8 ± 0.5 (3 runs)	343.1 ± 0.3[c] 338.1 ± 0.3[d] (3 runs)
$Cd(P(C_6H_5)_3)_2Cl_2$	131.6 ± 0.2 (7 runs)	198.9 ± 0.6 (6 runs)	413.0 ± 0.2[e] 406.1 ± 0.2[f] (7 runs)

[a] The C_{1s} line of triphenylphosphine was used to calibrate all runs. BE = 285.0 eV; $\beta\rho = 116.780$ for CH carbon using an aluminum anode; $\beta\rho = 104.500$ for CH carbon using a magnesium anode. [b] Ni $2p_{5/2}$. [c] Pd $3d_{3/2}$. [d] Pd $3d_{5/2}$. [e] Cd $3d_{3/2}$. [f] Cd $3d_{5/2}$.

was used for the palladium and cadmium complexes with ethanol as the solvent.

Triphenylphosphine was obtained from the City Chemical Co., New York, N. Y., and was used without further purification; mp 79–80°. *Anal.* Calcd for $C_{18}H_{15}P$: C, 82.44; H, 5.72; P, 11.83. Found: C, 82.49; H, 5.61; P, 11.59.

Triphenylphosphine oxide was obtained from Dr. D. E. Pearson, Vanderbilt University. It was first dissolved in ethanol and then precipitated by the addition of water. The precipitate was collected, dried, and finally sublimed *in vacuo* at 150°; mp 155–156°. *Anal.* Calcd for $C_{18}H_{15}PO$: C, 77.70; H, 5.40; P, 11.15. Found: C, 77.47; H, 5.46; P, 11.16.

Dichlorobis(triphenylphosphine)nickel(II).—A solution of $NiCl_2 \cdot 6H_2O$ (2.38 g, 0.01 mol) in 2 ml of H_2O was added to a solution of $(C_6H_5)_3P$ (5.25 g, 0.02 mol) in 250 ml of glacial acetic acid. The cloudy mixture was allowed to sit overnight in a refrigerator during which time dark blue-green crystals formed; yield 5.6 g (86%). *Anal.* Calcd for $NiC_{36}H_{30}P_2Cl_2$: C, 66.09; H, 4.62; Ni, 8.97. Found: C, 66.06; H, 4.64; Ni, 8.82.

Dichlorobis(triphenylphosphine)palladium(II).—A solution of triphenylphosphine (0.161 g, 0.0006 mol) in 50 ml of ethanol was added dropwise to a solution of K_2PdCl_4 (0.0971 g, 0.0003 mol) in 75 ml of ethanol with a minimum of water (<5 ml) to effect solution. A fine yellow solid precipitated immediately. This was filtered and washed consecutively with ethanol and water several times and then recrystallized from toluene; yield 0.199 g (95%). *Anal.* Calcd for $PdC_{36}H_{30}P_2Cl_2$: C, 61.59; H, 4.28; P, 8.83. Found: C, 61.52; H, 4.19; P, 8.67.

Dichlorobis(triphenylphosphine)cadmium(II).—Triphenylphosphine (1.2 g, 0.003 mol) in 100 ml of ethanol was added to a solution of anhydrous cadmium chloride (0.275 g, 0.0015 mol) in ethanol (30 ml) and water (5 ml). The resulting solution was cooled in a refrigerator for 1 hr, during which time the white crystalline product precipitated. The complex was recrystallized from 95% ethanol; yield 0.88 g (83%). *Anal.* Calcd for $C_{36}H_{30}P_2CdCl_2$: C, 61.07; H, 4.26; P, 8.76. Found: C, 60.91; H, 4.37; P, 8.68.

Results and Discussion

The results are of interest in showing how this technique can indicate information of an otherwise almost inaccessible type on the bonding in coordination compounds. The results are presented in Table I.

There are several aspects of the data which are quite striking. The first is that the difference between the phosphorus 2p bonding energies of the free and coordinated triphenylphosphine of the complexes studied is so small that there is considerable overlap of their experimental ranges. At first glance this would seem to indicate that the phosphorus lone pair is not significantly perturbed by coordination in these complexes, but this seems to be a rather unlikely possibility in view of the stability of the complexes. Upon examining the data carefully, it can be seen that the binding energies of the phosphorus 2p electrons of the complexes fall within a very narrow range. While this range does overlap the experimental range of the free triphenylphosphine, it seems significant that it is at the *low* energy end. This indicates a probable net drift of electron density *toward* the phosphorus atom in the complexes. Thus it can be seen that in each of the complexes studied, the binding energies of the phosphorus 2p electrons fall *at* or *below* the binding energy of the same electrons in the free triphenylphosphine, indicating that the total electron density around the phosphorus *remains the same or increases upon coordination.* Pelavin, Hendrickson, Hollander, and Jolly[5] reported data on two other coordination compounds of triphenylphosphine which fall very close to the range of the compounds studied here. Their value for the uncoordinated triphenylphosphine, on the other hand, differs from the values we obtained by 1.3 eV, which is outside our error limits. Pelavin, *et al.*, did not report error limits for their data. We can offer no explanation for this disagreement; however, other investigators in this laboratory[6] have found a value for uncoordinated triphenylphosphine which is within 0.2 eV of the value we report.

Since the lack of perturbation of the lone pair appears to be ruled out by the stability of the complexes, other effects must be considered. A possible explanation of the constancy of the electron density on the phosphorus atom in the complexes and the free triphenylphosphine is that opposing features of σ bonding ($P \rightarrow M$ donation) and π bonding ($M \rightarrow P$ donation) result in near cancellation of total electron drift and a negligible effect on the total electron density in the neighborhood of the phosphorus atom. Hendrickson, Hollander, and Jolly[7] have noted chemical shifts of nitrogen 1s electrons in a series of coordination compounds involving nitrogen ligands with π-acceptor orbitals, which they ascribe to this same $M \rightarrow L$ "back-bonding."

Both the tetrahedral (Ni[4b] and presumably Cd) and square-planar (Pd) complexes have at least two filled metal d orbitals of appropriate symmetry for the formation of π bonds with the phosphine ligands. In the case of the tetrahedral complexes, any appropriate pair may be used, while in the square-planar complex the filled d_{xz} and d_{yz} orbitals can be utilized. It is interesting and perhaps somewhat unexpected that the tetrahedral and square-planar complexes π bond to about the same extent, but indeed the experimental

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binding energies bear this out (*cf.* Table I). If the M→P π bonding were more important in the complex formation than the P→M σ bonding, the increased M→P donation would increase the electron density of the phosphorus and thus decrease the electron binding energy, which is exactly the effect noted. The very slight drop in binding energy of the phosphorus 2p electrons between free triphenylphosphine and triphenylphosphine in the complexes indicates that back-donation from the occupied d orbitals of the metal atoms probably occurs to a greater extent than the sharing of the phosphorus lone pair with the cadmium. Here the assumption must be made that the σ-bonding electrons have at least equal if not greater effect on core-electron binding energies than π-bonding electrons.

Another aspect of the data is the considerable shift which occurs when the phosphorus is bound to an oxygen, an element of very high electronegativity. In this case a σ and a π bond are also formed between the atoms[8,9] with the σ bond involving P→O and the π bond involving O→P donation. The significant shift here indicates a depletion of electron density from around the phosphorus atom. The high electronegativity of the oxygen atom leads directly to a low polarizability. The combination of high electronegativity and low polarizability could cause the oxygen to dominate the σ-bonding electrons while π bonding less efficiently and thus effect the drift of electron density away from the phosphorus.

Little can be said regarding the spectra of the coordinated chloride. The low polarizability of the chloride ion would lead one to expect very little change in the binding energy of the chlorine core electrons among similar complexes, and indeed a very constant value is obtained.

Since we are here concerned only with the relative binding energies of atoms within similar compounds, we assume that any solid-state interactions that might affect the data will be small and/or essentially invariant.

Spectra of this sort seem to be capable of providing a kind of information on bonding in complexes which allows a direct assessment of the relative importance of donation *via* σ bonds *vs.* back-donation from appropriate metal orbitals.

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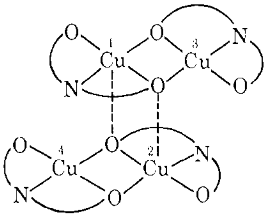
Correspondence

Exchange Coupling in Tetranuclear Complexes. The Model and Some of Its Limitations

Sir:

Recently Hatfield and Inman[1] set up a four-center exchange-coupled model to describe the magnetic properties of acetylacetonemono(*o*-hydroxyanil)copper(II), **1**, and its analogs. **1** had previously been treated as a dimer,[2] whose magnetic properties therefore followed the Bleaney–Bowers equation[3]



1

$$\chi_{\mathrm{Cu}} = \frac{Ng^2\beta^2}{kT}(3 + e^{-2J/kT})^{-1} + N\alpha \tag{1}$$

where the symbols have their usual meaning, but **1** is in fact a weakly linked tetramer.[4] The general treatment of such multinuclears involves a calculation outlined elsewhere,[5,6] specific results for which have been given for tri-, tetra-, and multinuclear interacting complexes.[5–7] The general results, applicable to complex **1**, based on a spin-only Heisenberg exchange model with all integrals J_{ij} (between the ith and jth spins) independent, have been given.[6] The Hamiltonian is

$$\mathcal{H} = -2\sum_{j>i=1}^{n} J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j \tag{2}$$

and the magnetic susceptibility is given by

$$\chi_{\mathrm{M}} = \frac{Ng^2\beta^2}{4kT} \times \frac{10e^{-E_2/kT} + 2e^{-E_1{}^{\mathrm{a}}/kT} + 2e^{-E_1{}^{\mathrm{b}}/kT} + 2e^{-E_1{}^{\mathrm{c}}/kT}}{5e^{-E_2/kT} + 3e^{-E_1{}^{\mathrm{a}}/kT} + 3e^{-E_1{}^{\mathrm{b}}/kT} + 3e^{-E_1{}^{\mathrm{c}}/kT} + e^{-E_0{}^{\alpha}/kT} + e^{-E_0{}^{\beta}/kT}} + N\alpha \tag{3}$$

where the E_2, etc., are the energies of the total spin states $S_{\mathrm{T}} = 2, 1, 1, 1, 0, 0$. The validity of the treatment of the multinuclear spin model is demonstrated by its ability to predict the results of the extended Kambe method,[5,6,8,9] but like all spin–spin coupling models its applicability is limited by experimental error, by the possibility of paramagnetic impurities,

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