Discussion

The chemistry and structural data for oxygen-carrying (μ-peroxo) cobalt–histidine complexes and related substances have been previously summarized.[10] In the present work, we have characterized the first known μ-superoxo-dicobalt ion containing histidine as ligands. The presence of this bridge is clearly indicated by both the optical spectrum (678-nm peak) and the epr characteristics.[10]
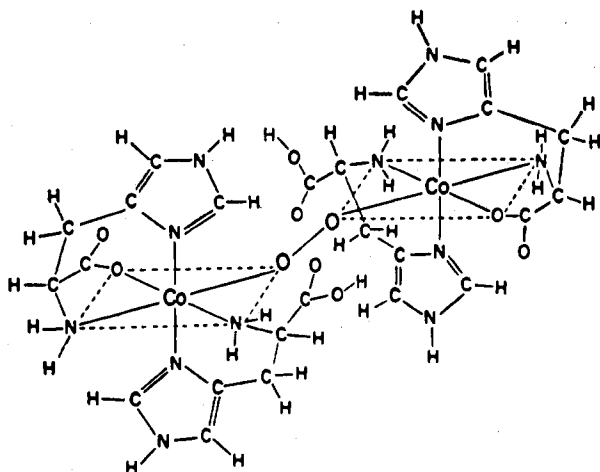

Figure 2.—The proposed structure of the μ-superoxo-bis[bis(L-histidinato)cobalt(III)](3+) ion.

The probable structure for the ion is shown in Figure 2, with the nitrogen atoms from the amine groups occurring cis to each other on each cobalt.[10,12]

Of particular interest in the infrared spectrum of the complex (Figure 1) is the strong band at 1740 cm^{-1} in the carbonyl region. This can be assigned to free carboxylic acid groups,[11] indicating that not all the histidine ligands are tridentate. The acidity of the complex dissolved in water also attests to the presence of such groups.

The reduction in acidic solution presumably goes *via* the one-electron step

$$[Co^{3+}O_2{}^-Co^{3+}] + HQ \longrightarrow [Co^{3+}O_2{}^{2-}Co^{3+}] + HQ^+$$

which is followed by internal charge transfer and oxygen release

$$[Co^{3+}O_2{}^{2-}Co^{3+}] \longrightarrow 2Co^{2+} + O_2$$
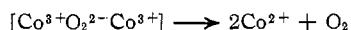
The latter process is known to occur with the μ-peroxo-dicobalt–ammine complex.[10]

Qualitative experiments indicate that D-histidine, DL-histidine, and histamine can also form superoxo-bridged dicobalt complexes.

(12) M. M. Harding and H. A. Long, *J. Chem. Soc. A*, 2554 (1968).

Photoelectron Spectroscopy of Coordination Compounds. III. A Comparison of Platinum(II) and Platinum(IV) Compounds

BY W. E. MODDEMAN, J. R. BLACKBURN, G. KUMAR,
K. A. MORGAN, R. G. ALBRIDGE, AND M. M. JONES*

We have previously published two reports[1,2] that describe the use of photoelectron spectroscopy to investigate the π-acceptor character of ligands in coordination compounds.[3] In our first study[1] we found that the 2p binding energy of phosphorus in triphenylphosphine does not increase upon coordination of the triphenylphosphine to nickel, palladium, or cadmium. We ascribe this to the fact that a coordinated phosphorus atom not only donates an electron lone pair to a ligand–metal σ bond but also accepts a compensating amount of charge from the metal *via* π bonding. Similar neutralization of electron transfer between platinum and phosphorus of triphenylphosphine was inferred by Cook, *et al.*,[4] for $Pt[P(C_6H_5)_3]_4$ in their comparison of Pt 4f binding energies for platinum coordinated to a number of π-bonding ligands. More recently we have presented more definitive arguments regarding the π-acceptor nature of ligands in a report on the inner-orbital shifts of both the metal and the ligand in a series of palladium complexes.[2] For those complexes containing only halide ligands, which are not π acceptors,[5] we observed that the palladium 3d binding energy is proportional to the palladium charge, estimated by means of electronegativity differences. For those complexes containing cyano ligands, which are known to be effective π-acceptor ligands,[6] the palladium 3d binding energy was found to be considerably larger than expected from simple charge calculations.

In the present paper we have examined some potassium salts of four- and six-coordinated platinum compounds in an effort to compare platinum chemical shifts with the shifts previously measured for the palladium compounds.[2] In addition, shifts were measured for the metal and the ligands in halo–cyano and halo–nitro complexes, in which the halides are σ donors and the cyano or nitro groups are π acceptors as well as σ donors. Data on such mixed-ligand compounds, when compared with data on complexes containing only one type of ligand, may provide a better understanding of ligand–metal bonding. The two series of compounds used for these mixed-ligand studies

(1) J. R. Blackburn, R. Nordberg, F. Stevie, R. G. Albridge, and M. M. Jones, *Inorg. Chem.*, **9**, 2374 (1970).

(2) G. Kumar, J. R. Blackburn, R. G. Albridge, W. E. Moddeman, and M. M. Jones, *ibid.*, **11**, 296 (1972).

(3) L. D. Pettit, *Quart. Rev., Chem. Soc.*, **25**, 1 (1971).

(4) C. D. Cook, K. Y. Wan, U. Gelius, K. Hamrin, G. Johansson, E. Olsson, H. Siegbahn, C. Nordling, and K. Siegbahn, *J. Amer. Chem. Soc.*, **93**, 1904 (1971).

(5) The halide ligands do have available empty d orbitals for back-bonding; however, metal electron delocalization into these π-acceptor orbitals is small. For this reason the halides are considered to be only σ-donor ligands.

(6) L. H. Jones, *Inorg. Chem.*, **2**, 777 (1963); **3**, 1581 (1964), and references therein.

were (1) K_2PtCl_4, K_2PtBr_4, $K_2Pt(NO_2)_4$, $K_2Pt(NO_2)_4Cl_2$, $K_2Pt(NO_2)_4Br_2$, $K_2Pt(NO_2)_6$; and (2) K_2PtCl_4, K_2PtBr_4, $K_2Pt(CN)_4$, $K_2Pt(CN)_4Cl_2$, $K_2Pt(CN)_4ClBr$, $K_2Pt(CN)_4Br_2$, $K_2Pt(CN)_6$.

Experimental Section

Measurements were made with a 35-cm, iron-free, double-focusing magnetic electron spectrometer. This computer-regulated instrument has been described elsewhere.[7] Powdered samples were mounted on one side of a double-faced tape which was stuck to an aluminum sample holder. Mg $K\alpha$ radiation was used and the spectrometer was set at an instrumental energy resolution of *ca.* 0.15%. Typical line widths were as follows: Pt(4f), 2.2 eV; Br(3p), 3.4 eV; Cl(2p), 3.2 eV; K(2p), 2.2 eV; Pb(4f$_{7/2}$), 2.0 eV.

PbO was mixed with each platinum-containing compound in a 1:2 ratio and the Pb(4f$_{7/2}$) photoelectron line was used as an energy reference. This line was chosen because it lies close in energy to the 4f doublet of platinum. By standardizing against the C(1s) line of $[P(C_6H_5)_3]_2PdBr_2$, we determined the magnetic rigidity of the Pb(4f)(Mg $K\alpha$) photoline of PbO to be 112.415 G cm, taking the C(1s) binding energy to be 285.0 eV.[8]

The preparation and characterization of the platinum complexes used here, with the exception of PtCl$_2$, KPt(C$_2$H$_4$)Cl$_3$, and K$_2$Pt(CN)$_4$BrCl, have been published elsewhere.[9] The PtCl$_2$ was obtained from Alfa Inorganics, Inc.; the KPt(C$_2$H$_4$)Cl$_3$ was made by the reaction of K$_2$PtCl$_6$ and C$_2$H$_5$OH. *Anal.* Calcd for KPt(C$_2$H$_4$)Cl$_3$: C, 6.51; H, 1.11; Cl, 28.89. Found: C, 6.60; H, 1.28; Cl, 29.03.

Results and Discussion

Table I lists the measured shifts in the 4f$_{7/2}$ orbital of platinum for the element and 14 of its compounds. The shifts are measured relative to the 4f$_{7/2}$ binding energy for the pure metal which we determined to be 72.0 ± 0.2 eV. Also presented in Table I are the shifts re-

TABLE I
BINDING ENERGY SHIFTS IN THE 4f$_{7/2}$ LEVEL OF PLATINUM[a]

	Binding energy shifts, eV	
Compd	Pt 4f$_{7/2}$	Pd 3d$_{5/2}$
M	0	0
MCl$_2$	2.3 (2)	2.2 (4)
K$_2$MCl$_4$	2.4 (3)	2.7 (3)
K$_2$MCl$_6$	4.8 (2)	4.6 (3)
K$_2$MBr$_4$	1.7 (2)	1.8 (3)
K$_2$M(NO$_2$)$_4$	2.8 (2)	3.5 (3)
K$_2$M(CN)$_4$	2.0 (3)	3.5 (3)
KPt(C$_2$H$_4$)Cl$_3$	2.6 (3)	
K$_2$PtBr$_6$	3.8 (3)	
K$_2$Pt(CN)$_6$	4.2 (3)	
K$_2$Pt(NO$_2$)$_6$	4.5 (3)	
K$_2$Pt(CN)$_4$Cl$_2$	4.8 (3)	
K$_2$Pt(CN)$_4$Br$_2$	4.5 (3)	
K$_2$Pt(CN)$_4$BrCl	4.6 (3)	
K$_2$Pt(NO$_2$)$_4$Cl$_2$	4.7 (3)	
K$_2$Pt(NO$_2$)$_4$Br$_2$	4.4 (3)	

ported earlier[2] for corresponding palladium complexes. It is of interest to compare the platinum data with the palladium data because the elements are chemically similar and have been assigned the same electronegativity;[10] hence, observed differences in the data might be attributed to other considerations such as the difference in the ionic radii.

In Figure 1 the chemical shifts of palladium are plotted against those of platinum for corresponding
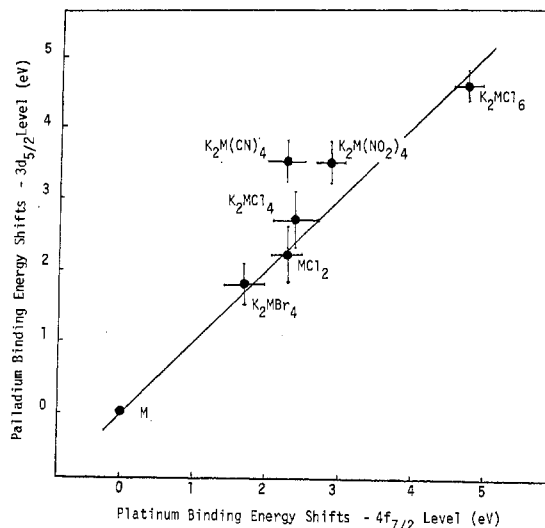
(7) A. Fahlman, R. G. Albridge, R. Nordberg, and W. M. LaCasse, *Rev. Sci. Instrum.*, **41**, 596 (1970).

(8) U. Gelius, P. F. Heden, J. Hedman, B. J. Lindberg, R. Manne, R. Nordberg, C. Nordling, and K. Siegbahn, *Phys. Scr.*, **2**, 70 (1970).

(9) K. A. Morgan, Ph.D. Thesis, Vanderbilt University, 1971.

(10) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

Figure 1.—A plot of palladium binding energy shifts *vs.* platinum binding energy shifts.

compounds.[11] For those compounds containing only halide ligands, the data fall on a straight line with a slope of unity. The points for the complexes containing cyano or nitro ligands fall well above the straight line. In the halide ligands, for which π bonding is assumed to be unimportant, the charge distribution between ligand and metal appears to be determined by electronegativity differences, which are the same for the palladium and platinum complexes. For the cyano and nitro ligands, which do π bond, the Lewis-acid character of the ligand in this bonding increases the orbital binding energies of the metals above that expected from electronegativity considerations. That the increase is larger for palladium than for platinum can perhaps be explained by the fact that palladium has the smaller ionic radius,[12] by about 0.10 Å, and thus allows more π-orbital overlap and more M → L charge transfer. The fact that the measured[13] CN stretching frequencies for square-planar, hydrated K$_2$M(CN)$_4$·xH$_2$O (M = Ni, Pd, Pt) increase with increasing atomic number of M is in agreement with our interpretation of the photoelectron data.[14]

We previously interpreted our palladium data in terms of molecules composed of charged atoms, and we ignored all contributions to the molecular potential except those of nearest-neighbor atoms. Such a model had been used before to qualitatively explain photoelectron data for a number of low-z elements.[15] Furthermore, Schwartz[16] has demonstrated the validity of the charged-atom concept for a number of simple low-z, free molecules by showing that the shifts in the calculated inner-shell eigenvalue energies are equal

(11) The electrostatic model upon which we base our interpretation predicts equal shifts for all core electrons providing the valence electrons do not penetrate the core. Therefore, we compare shifts in the 4f level of platinum to shifts in the 3d level of palladium under the reasonable assumption that the 5d and 4d valence electrons of platinum and palladium have negligible penetration.

(12) C. S. G. Phillips and R. J. P. Williams, "Inorganic Chemistry," Vol. II, Oxford University Press, Oxford, 1966, pp 241–242.

(13) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley, New York, N. Y., 1970, and references therein.

(14) M. F. A. El-Sayed and R. K. Sheline, *J. Inorg. Nucl. Chem.*, **6**, 187 (1958).

(15) See, for example, ESCA: K. Siegbahn, *et al.*, *Nova Acta Regiae Soc. Sci. Upsal.*, **4**, 20 (1967).

(16) M. E. Schwartz, *Chem. Phys. Lett.*, **6**, 631 (1970).

TABLE II
BINDING ENERGY SHIFTS BETWEEN
PLATINUM(II) AND PLATINUM(IV) COMPLEXES[a]

Compd	Shift, eV	Compd	Shift, eV
1, A = B = Cl	2.4	6, A = NO₂, B = Br	1.6
2, A = CN, B = Cl	2.8	7, A = CN, B = Br, Cl	2.6
3, A = NO₂, B = Cl	1.9	8, A = B = CN	2.2
4, A = B = Br	2.1	9, A = B = NO₂	1.7
5, A = CN, B = Br	2.5		

[a] The shift recorded is the binding energy of the Pt $4f_{7/2}$ level for the IV complex minus that for the II complex. The compounds are identified by listing A and B for the general formulas K_2PtA_4 and $K_2PtA_4B_2$.

to the shifts in the quantum mechanically calculated molecular potential. Our attempt to use an oversimplified and classical model to interpret data for molecular solids of intermediate-z elements embraces the following difficulties: relativistic and correlation effects were ignored, work functions were ignored, molecular and crystal potentials were ignored, and the applicability of Koopmans' theorem was tacitly assumed. The concern is not the absolute magnitude of the effects themselves but the size of the differential effects encountered when data for similar molecules are compared. For example, the relativistic corrections for the platinum 4f and the palladium 3d orbitals are *ca.* 4 and 5 eV,[17] respectively, but presumably the differential corrections for, say, K_2PdCl_4 and K_2PdCl_6 are much smaller. Unfortunately, the task of determining the size of all of these differential effects would be an enormous one.

For these reasons we have chosen not to correlate our platinum data to calculated charges but rather to compare directly the empirical data for platinum to the empirical data for palladium. The resulting straight line with slope unity indicates that the effects discussed above at least do not occur in a fashion that causes the data to scatter. Even without an interpretive model one can see directly that the compounds containing the cyano and nitro ligands are in some way special. Our explanation of the deviations based upon the simplistic charged-atom model is consistent with the data and with the known character of cyano and nitro groups.

We have investigated also the differences between the platinum binding energy for platinum(II) and platinum(IV) complexes. These differences can be determined from the data in Table I and, for convenience, are summarized in Table II. The shifts listed are the platinum $4f_{7/2}$ binding energy of the Pt(IV) complex $(K_3PtA_4B_2)$ minus that of the Pt(II) complex (K_2PtA_4), where A and B are general symbols representing Cl, Br, CN, or NO₂. The addition of ligands B to a Pt(II) complex to form a Pt(IV) complex causes an increase in the platinum $4f_{7/2}$ binding energy; however, the increase caused by a given B is not the same for all of the Pt(II) complexes. For example, the addition of chlorine to K_2PtA_4 to form $K_2PtA_4Cl_2$ causes shifts of 2.4, 2.8, and 1.9 eV for A = Cl, CN, and NO₂, respectively. Similarly, the addition of bromine to form $K_2PtA_4Br_2$ creates shifts of 2.1, 2.5, and 1.6 eV for A = Br, CN, and NO₂, respectively. It is interesting to note that, for the six compounds discussed above, the

TABLE III
BINDING ENERGIES FOR THE K 2p, THE Cl 2p,
AND THE Br 3p LEVELS

No.	Compd	Binding energy, eV		
		K 2p	Cl 2p	Br 3p
1	KCl	295.7	201.2	
2	K₂PtCl₄	294.8	200.7	
3	K₂PtCl₆	295.1	201.0	
4	PtCl₂		201.1	
5	K₂PtCl₃(C₂H₄)	294.8	200.5	
6	KBr	295.3		184.1
7	K₂PtBr₄	294.7		183.8
8	K₂PtBr₆	294.5		183.5
9	K₂Pt(CN)₄	294.2		
10	K₂Pt(CN)₆	294.2		
11	K₂Pt(CN)₄Cl₂	294.3	200.4	
12	K₂Pt(CN)₄Br₂	294.3		183.6
13	K₂Pt(CN)₄ClBr	294.2	200.4	184.0
14	K₂Pt(NO₂)₄	294.3		
15	K₂Pt(NO₂)₆	294.0		
16	K₂Pt(NO₂)₄Cl₂	294.0	200.2	

shifts caused by the addition of chlorine is in all cases 0.3 eV greater than that caused by the addition of bromine.

Table III lists the potassium 2p, the chlorine 2p, and the bromine 3p binding energies for the complexes studied and for the salts KCl and KBr. In a previous paper[2] we have reported that the bridged bromide in PdBr₂ has a larger binding energy than does the coordinated bromide in K₂PdBr₂. We rationalized from a simple charged-shell model that a bridged halide, attached to two Pd(II) ions, would be more positively charged than a coordinated halide, attached to only one Pd(II) ion. Clark, *et al.*,[18] noted a 1-eV difference between terminal and bridging chlorides in $L_2M_2Cl_4$ complexes; however, they interpreted the bridging chloride to have the smaller binding energy. To determine the possible applicability of photoelectron spectroscopy to the identification of uncoordinated, coordinated, and bridged halides we compare here the chlorine 2p binding energy in KCl, K₂PtCl₄, K₂PtCl₆, and PtCl₂ (compounds 1–4 in Table III). From the charged-shell model we might expect an increase in the halide binding energy going through the series from complex 1 to complex 4. Indeed, the binding energy of the chloride in PtCl₂ is greater than that for either of the coordinated species, K₂PtCl₄ or K₂PtCl₆; however, contrary to our expectations, the chloride in KCl has the highest binding energy of all. This result might be due to crystal field effects which should be different for the three different types of compounds under discussion. If we assume that the observed differences in the K 2p binding energy are due to crystal field effects and for compounds 1–3 normalize the K 2p and Cl 2p data to a value of 294.8 eV for the K 2p binding energy, then the adjusted Cl 2p binding energies are 200.3, 200.7, and 200.7 eV for KCl, K₂PtCl₄, K₂PtCl₆, respectively. These results indicate a net difference no greater than 0.4 eV between the coordinated and uncoordinated chloride. A similar adjustment for the compounds KBr, K₂PtBr₄, and K₂PtBr₆ indicates a net difference no greater than about 0.3 eV between the coordinated and uncoordinated bromide.

(17) F. Herman and S. Skillman, "Atomic Structure Calculations," Prentice-Hall, Englewood Cliffs, N. J., 1963.

(18) D. T. Clark, D. Briggs, and D. B. Adams, submitted for publication.