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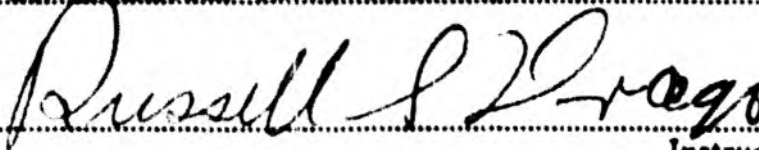
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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

.....
LOUIS JAMES DIZIKES.....
ENTITLED Infrared and Electronic Spectroscopic, NMR Contact Shift.....
Study of some Pyridine, Substituted Pyridine, and Substituted.....
Acetate Bis-Stilbenediamine Nickel (II) Complexes.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF..... BACHELOR OF SCIENCE

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INFRARED AND ELECTRONIC SPECTROSCOPIC,
NMR CONTACT SHIFT STUDY OF SOME PYRIDINE,
SUBSTITUTED PYRIDINE,
AND SUBSTITUTED ACETATE BIS-STILBENEDIAMINE NICKEL (II) COMPLEXES.

BY

LOUIS JAMES DIZIKES

THESIS

FOR THE

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Infrared and Electronic Spectroscopic, Nmr Contact Shift
Study of Some Pyridine, Substituted Pyridine, and Substi-
tuted Acetate Bis-stilbenediamine Nickel (II) Complexes.

1. Introduction

The intention of this study was to first prepare a series of paramagnetic complexes of the type $\text{trans-Ni}(\text{meso-stilbenediamine})_2(\text{L})_2(\text{BF}_4)_2$, where L is a neutral, monodentate ligand and stilbene-diamine's molecular formula is $\text{C}_{14}\text{H}_{16}\text{N}_2$. Pyridine and various substituted pyridines were to be used mainly for the ligand, L, in these complexes. The idea was to use pyridine and the liquid substituted pyridines as solvents for the $\text{Ni}(\text{meso-stilbenediamine})_2(\text{BF}_4)_2$ complex and to get the solvent to coordinate to the nickel (II) complex in the axial positions.

The second part of this study involved preparing a series of paramagnetic complexes of the type $\text{trans-Ni}(\text{meso-stilbenediamine})_2(\text{anion})_2$, where the anion was a series of substituted acetates: monobromoacetate, tribromoacetate, and moniodoacetate. Both series of paramagnetic complexes were to be investigated using nmr, IR, and visible spectroscopy as done by Jeffrey I. Zink and Russell S. Drago for acetate, chloro-substituted acetate, benzoate, and substituted benzoate anions.¹

It was desirable for the complexes studied to be tetragonal distortions of octahedral complexes. The tetragonal distortion reducing the effective symmetry of the ligand field from O_h to D_{4h} . In the nickel (II) complexes to be studied, the tetragonal distortion occurred because the two ligands in the trans-positions were electrically different from the two bidentate stilbenediamine ligands. When the tetragonal distortion was strong, the first absorption band, ${}^3A_{2g} \rightarrow {}^3T_{2g}$

split into two components because of the splitting of the ${}^3T_{2g}(F)$ state into two states, 3E_g and ${}^3B_{2g}$. Under strong tetragonal distortion, the higher energy states ${}^3T_{1g}(F)$ and ${}^3T_{1g}(P)$ also split due to the decrease in symmetry from O_h to D_{4h} , ${}^3T_{1g}(F)$ going to ${}^3A_{2g}(F)$ and ${}^3E_g(F)$ and ${}^3T_{1g}(P)$ going to ${}^3A_{2g}(P)$ and ${}^3E_g(P)$ (see figure 1). Near-infrared and visible absorption spectroscopy was carried out to determine the magnitude of the tetragonal distortion of the various complexes.^{2,3}

A diamagnetic-paramagnetic isomerism between yellow and blue forms of nickel (II) complexes was found by Lifschitz for C-substituted ethylenediamines in complexes of the form $Ni(Sen)_2X_2$ where Sen = substituted ethylenediamine and X = monovalent anion. The $Ni(Sen)X_2$ complexes were found in both the blue and the yellow forms with and without water. The forms were found to convert into each other under various conditions with only one regular feature, the blue compounds were paramagnetic and the yellow compounds were diamagnetic.⁴ Some of the blue compounds were readily found to be the result of tetragonally distorted octahedral fields. This result indicates that the anions might be coordinated to the nickel in the paramagnetic, blue forms while in the diamagnetic, yellow forms the anions are not coordinated to the nickel. The ease of conversion from the one form to the other being effected perhaps by a very small change in the distance of the anion from metal.⁵ Higginson, Nyburg, and Wood⁶ also found that color changes in complexes of the type $Ni(\text{meso-stein})_2(RCOO)_2$, where R = H, CH₃, CH₂Cl, CHCl₂, and CCl₃, were accompanied by a corresponding change in magnetic property, and that $Ni(\text{stein})_2(Cl_2CHCO_2)_2$ possesses a diamagnetic-paramagnetic equilibrium in some solvents. In chloroform and acetone the complex

was tetragonally coordinated and paramagnetic. Nyburg and Wood⁷ found that for the dichloroacetate the blue crystals contained only octahedrally coordinated nickel while the yellow crystals contained both paramagnetic octahedrally coordinated nickel and diamagnetic planar four-coordinate nickel in a 2:1 ratio in solid crystals.

"In the yellow diamagnetic complexes the effective axial ligand field is zero and the strong in-plane ligand field, due to the diamine molecules, causes the singlet $^1A_{1g}$ state to be the ground state whereas in the blue octahedral complexes, the axial ligand field stabilizes the triplet $^3A_{2g}$ state (assuming a ligand field of O_h symmetry) and the complexes are paramagnetic."⁷

The Nickel (II) complexes were desired to be paramagnetic so that the proton magnetic resonance contact shift could be measured. "Unpaired electrons in orbitals which have a finite existence at the magnetic nucleus affect the nmr spectrum of that nucleus through both relaxation broadening and a large shift in the position of resonance. The requisite condition for observing the nmr of a paramagnetic compound is that either or both $1/T_e > A_n$ and $1/T_c > A_n$ is fulfilled, where $1/T_e$ is the rate of electron spin relaxation, $1/T_c$ is the rate of chemical exchange, and A_n is the unpaired electron spin-nuclear spin coupling constant. Contact nmr shifts arise from the effects due to the small population difference in the electron spin states."⁸ For paramagnetic, nickel (II) complexes, the electron spin relaxation or ligand-exchange rates of these transition metal compounds in solution is sufficiently fast so as to allow observation of the nmr spectra of ligand nuclei. The shifts in the nmr arising from electron spin-nuclear spin coupling are called contact shifts.

ii. Experimental

Meso Stilbenediamine (stein)--the ligand was prepared as by Irving and Parkins.¹¹

Ammonium acetate (120 g.) was boiled under reflux with 300 ml. benzaldehyde for 4 hours. The solution turned yellow and a thick white precipitate formed. The precipitate was washed with ethanol until all the yellow was washed from the white N'-benzoyl-N'-benzylidene-meso-1,2-diphenylethylenediamine. The white precipitate was then heated with 100 ml. of water and 54 ml. of concentrated sulphuric acid, and steam was passed through the solution for 6 hours. The steam removes the excess benzoic acid and benzaldehyde. The product is then cooled and filtered and the filtrate is neutralized slowly with ammonia with ice cooling giving the flaky white mesostilbenediamine precipitate. The white precipitate was recrystallized from petroleum ether (b.p. 60-80°C) and dried over P₂O₅.

Calc. for C₁₄H₁₆N₂: C, 79.25; H, 7.55; N, 13.21

Found for C₁₄H₁₆N₂: C, 79.04; H, 7.41; N, 12.89

Ni(meso-stein)₂(BF₄)₂--yellow-orange complex

About one-fourth of the meso-stilbenediamine was dissolved in ethyl alcohol and to this solution was added an excess of nickel tetrafluoroborate dissolved in ethyl alcohol. The resulting solution was yellow-green in color and upon cooling in an ice bath yielded yellow-orange crystals of Ni(stein)₂(BF₄)₂. The crystals were collected by filtration, washed with 25 ml. cold ethyl alcohol, and dried "in vacuo" over P₂O₅ for 10 hours.

Calc. for C₂₈H₃₂N₄F₈B₂Ni: C, 51.2; H, 4.93; N, 8.55

Found for C₂₈H₃₂N₄F₈B₂Ni: C, 52.3; H, 5.41; N, 8.57

Ni(ms-stein)₂(py)₂(BF₄)₂--violet complex

Ni(ms-stein)₂(BF₄)₂ (1.0g.) was dissolved in hot pyridine (5 ml.). On standing for 24 hours violet crystals of the complex were formed. The crystals were collected by filtration and dried "in vacuo" over P₂O₅ for 24 hours.

Calc. for C₃₈H₄₂N₆F₈B₂Ni: C, 55.99; H, 5.19; N, 10.31; Ni, 7.20

Found for C₃₈H₄₂N₆F₈B₂Ni: C, 57.30; H, 5.36; N, 10.28; Ni, 6.61

Ni(ms-stein)₂(4-picoline)₂(BF₄)₂--blue-green complex

Ni(ms-stein)₂(BF₄)₂ (1.0g.) was dissolved in hot 4-picoline (5 ml.). On standing for 24 hours a sticky violet mass was formed. The sticky substance was dried "in vacuo" over P₂O₅ for 48 hours. Blue-green crystals remained after the 48 hours.

Calc. for C₄₀H₄₆N₆F₈B₂Ni: C, 56.98; H, 5.50; N, 9.97; Ni, 6.96

Found for C₄₀H₄₆N₆F₈B₂Ni: C, 58.53; H, 5.89; N, 10.52; Ni, 5.74

Ni(ms-stein)₂(3-Cl-py)₂(BF₄)₂--bright yellow-complex

Ni(ms-stein)₂(BF₄)₂ (1.0g.) was dissolved in hot 3-chloropyridine (5 ml.). On standing for 24 hours, bright yellow crystals of the complex were formed. Attempts at recrystallization in ethanol and chloroform still yielded bright yellow crystals.

Ni(ms-stein)₂(picolinic acid)₂(BF₄)₂--pale blue crystals

Ni(ms-stein)₂(BF₄)₂ (1.0g.) was added to hot dimethyl sulfoxide yielding a yellow solution. Picolinic acid was then added to this hot solution until the solution was completely blue in color. After concentrating the solution and drying it "in vacuo" over P₂O₅ the pale blue complex was left. The complex was recrystallized from hot

ethanol and dried "in vacuo" over P_2O_5 for 24 hours.

Calc. for $\text{C}_{40}\text{H}_{42}\text{N}_6\text{F}_8\text{B}_2\text{Ni}$: C, 53.19; H, 4.68; N, 9.30; Ni, 6.49

Found for $\text{C}_{40}\text{H}_{42}\text{N}_6\text{F}_8\text{B}_2\text{Ni}$: C, 48.86; H, 5.51; N, 7.12; Ni, 4.14

III. Discussion

In the second part the three compounds desired were $\text{Ni}(\text{stein})_2(\text{BrCH}_2\text{CO}_2)_2$, $\text{Ni}(\text{stein})_2(\text{CBr}_3\text{CO}_2)_2$, and $\text{Ni}(\text{stein})_2(\text{ICH}_2\text{CO}_2)_2$. In order to observe the contact shift in the nmr, the compounds desired needed to be paramagnetic and would have the blue color characteristic of these paramagnetic nickel compounds as opposed to being orange or yellow which is characteristic of diamagnetism in these complexes. The basic methods were used in trying to get the three compounds; but neither method was successful except in one case.

The first method used was to dissolve some of the $\text{Ni}(\text{stein})_2(\text{BF}_4)_2$ complex in ethanol and add to it a drop at a time a water solution of one of the substituted acetates which had been made by dissolving the substituted acetic acid in water and neutralizing the solution with NaOH until only a very slightly acid solution remained. A basic solution would yield nickel hydroxide upon addition to the $\text{Ni}(\text{stein})_2(\text{BF}_4)_2$. The substituted acetate was added dropwise until the ethanol solution of $\text{Ni}(\text{stein})_2(\text{BF}_4)_2$ went from orange to green. Upon stirring only the monobromoacetate solution turned cloudy blue. The monoiodoacetate solution upon stirring became basic and orange in color. Concentration yielded yellow-orange crystals. The cloudy blue monobromoacetate solution upon concentration yielded blue-violet crystals and a white impurity. The blue crystals and impurity could not be separated very well, both being soluble in ethanol and hot chloroform but not soluble in water, cold chloroform, or acetone. Quantitative analysis suggests that the blue-violet crystals weren't $\text{Ni}(\text{stein})_2(\text{BrCH}_2\text{CO}_2)_2$ but rather $\text{Ni}(\text{stein})_3(\text{BF}_4)_2$. The difference between calculated and actual yield of carbon being less than 2% in the latter complex. The

yellow-orange crystals yielded from the moniodoacetate and tribromoacetate solutions were found to be $\text{Ni}(\text{stein})_2 (\text{BF}_4)_2$. Very little or no complexing had occurred in the cases of the moniodoacetate and tribromoacetate.

A second part of this method involved doing a chloroform extraction on the monobromoacetate solution. After adding the monobromoacetate to the $\text{Ni}(\text{stein})_2 (\text{BF}_4)_2$, add first water with stirring then chloroform and heat with stirring. The dark green color of the water-ethanol layer gradually fades while the chloroform layer turns blue. After draining off the water-ethanol solution, the chloroform solution was then concentrated to a bright blue solution but yielded blue-green crystals. Dissolving these crystals in ethanol yielded a violet solution and upon concentration blue-violet crystals which when analyzed again seemed to be $\text{Ni}(\text{stein})_3 (\text{BF}_4)_2$ and not $\text{Ni}(\text{stein})_2 (\text{BrCH}_2\text{CO}_2)_2$.

The second method used eliminated the need for sodium and tetrafluoroborate ions. NiCO_3 was stirred and heated in water with the addition of one of the substituted acetic acids yielding $\text{Ni}(\text{BrCH}_2\text{CO}_2)_2$, $\text{Ni}(\text{ICH}_2\text{CO}_2)_2$ or $\text{Ni}(\text{CBr}_3\text{CO}_2)_2$. The reaction with the evolution of CO_2 gas readily occurred except in the case of $\text{CBr}_3\text{CO}_2\text{H}$ where very little of the $\text{Ni}(\text{CBr}_3\text{CO}_2)_2$ formed even after several hours of heating and stirring. Some stilbenediamine was then dissolved in ethanol and to it dropwise with stirring, was added one of the $\text{Ni}(\text{sub-acetate})_2$ solutions. The solution of stilbenediamine and $\text{Ni}(\text{CBr}_3\text{CO}_2)_2$ was initially green in color but turned orange and yielded after concentration and cooling in an ice bath yellow-orange crystals which appeared to be square planar $\text{Ni}(\text{stein})_2 (\text{CBr}_3\text{CO}_2)_2$. The solution of stilbenediamine and $\text{Ni}(\text{ICH}_2\text{CO}_2)_2$ was first a green solution but gradually turned bright blue as it was concentrated.

This solution yielded blue crystals within an hour of cooling in an ice bath. The color of the crystals was definitely different from the $\text{Ni}(\text{stein})_3 (\text{BF}_4)_2$ and it is believed they were $\text{Ni}(\text{stein})_2 (\text{ICH}_2\text{CO}_2)_2$. However, upon waiting another hour before collecting these crystals, a white impurity also precipitated. Attempts at recrystallization from ethanol always yielded the white impurity along with the blue crystals. The solution of stilbenediamine and $\text{Ni}(\text{BrCH}_2\text{CO}_2)_2$ yielded a green solution which after heating with stirring, concentrating, and cooling in an ice bath became a blue-green color yielding only orange crystals.

In the first part of the study, some of the $\text{Ni}(\underline{\text{ms-stein}})_2 (\text{py})_2 (\text{BF}_4)_2$ was ground in Kel-F stopcock grease until a fine partial size was obtained. The resulting mud was placed between two glass plates which were taped together and then taped to the metal holder which was immersed in a special dewar filled with liquid nitrogen. Spectrophotometric measurements were to be obtained on the $\text{Ni}(\underline{\text{ms-stein}})_2 (\text{py})_2 (\text{BF}_4)_2$ in the near-infrared and visible light regions by using the above mentioned apparatus and a Cary spectrophotometer, Model 14R1, equipped with a high-intensity source to get the desired absorption spectra in the near-infrared and visible regions. A piece of filter paper saturated with Nujol was placed in the reference beam. A beam attenuator was used to bring the pen onto the paper. The absorption spectra was to be used to measure the amount of splitting of the ${}^3\text{T}_{2g}(\text{F})$, ${}^3\text{T}_{1g}(\text{F})$, and ${}^3\text{T}_{1g}(\text{P})$ states due to the reduction in symmetry from O_h to D_{4h} . The result however was that very little or no reduction in symmetry had occurred as there was no splitting of the O_h states. Pyridine proved to be very close to stilbenediamine in electrical properties, as far as both being ligands bonded to a Ni(II) ion. Since there was no reduction

in symmetry from O_h to D_{4h} , there was also no tetragonal distortion of the octahedral ligand for the pyridine complex.

This part of the study, a series of substituted pyridine complexes, was not continued as 4-picoline would not have ligand properties significantly different from pyridine and neither would α -picoline or β -picoline. 3-chloropyridine when complexed with the $Ni(\underline{m} - \text{stein})_2 (BF_4)_2$ resulted in a yellow, diamagnetic complex not suitable for nmr contact shift study. Finally the complex with picolinic acid was blue in color and seemingly paramagnetic, but could not be completely purified and could not be used as part of a series study.

For these reasons a new series was chosen. The second series was not made by using the solvent to coordinate to the nickel but was to use chloroform and ethyl alcohol as solvents and monobromoacetate, moniodoacetate, and tribromoacetate as ligands. The object was to continue the study of J. I. Zink and R. S. Drago,¹ that is, investigate the relative strengths of a series of axial anionic ligands, and compare those results obtained by visible and IR spectroscopy with those obtained by nmr contact shift studies and the reasoning of the "ligand inductive effect." Zink and Drago found that as the axial ligand strength increased, the stilbenediamine proton magnetic resonance contact shift also increased which is opposite to what would be predicted by the inductive properties of the axial ligands. The "ligand inductive effect" is quite straight forward and states that as the axial ligand strength increases (i.e. higher D_{qz}), the formal charge on the metal ion decreases and D_{qz} also decreases. Previous studies^{12, 13, 14, 15} used this reasoning to explain their observed proton magnetic resonance contact shifts for the equatorial ligand protons.¹ The reasoning goes; as D_{qz} increases, D_{qxy} decreases

and, the metal-ligand bond strength decreases so would the amount of mixing of the metal ion and equatorial ligand orbitals also decrease. In the work of Zink and Drago, the proton contact shifts are not those predicted from this line of reasoning. Zink and Drago found that as the axial ligand strength increased, the proton contact shift also increases. The nickel-oxygen bond strength and the order of relative coordinating power of the anions in the Zink-Drago acetate series was: acetate > monochloroacetate > dichloroacetate > trichloroacetate.

The increase in axial ligand strength with a corresponding increase in the proton contact shift is explained qualitatively by a molecular orbital approach.¹ By this approach, as the strengths of the axial and equatorial ligands become more equal, the splitting of the e_g levels becomes smaller with a corresponding decrease in the energy difference between the ligand orbital and the $d_{x^2-y^2}$ metal orbital (see figure 2) resulting in more mixing of the orbitals instead of less as predicted by the "ligand inductive effect."

As was explained earlier, the desired complexes of mono- and tribromoacetate and moniodoacetate could not be made. The second method of preparation as described in the experimental section of this thesis did yield some positive results and it is suggested that this method be used for the preparation of $Ni(stein)_2 (BrCH_2CO_2)_2$ and $Ni(stein)_2 (ICH_2CO_2)_2$ being careful not to use an excess of either $Ni(BrCH_2CO_2)_2$ or $Ni(ICH_2CO_2)_2$ in the preparation. The tribromoacetic acid would not react substantially with the $NiCO_3$ so a steric effect may be contributing to the fact that tribromoacetate ion is a weak ligand and together they may be enough to keep it from complexing at all. On the basis of pK values (Table I), the order of relative coordinating power for these

anions would be: monoiodoacetate > monobromoacetate > tribromoacetate.

Though no new compounds were successfully prepared a proton magnetic resonance contact shift was obtained for $\text{Ni}(\text{stein})_2 (\text{Cl}_3\text{CCO}_2)_2$. This spectra was obtained by using a Jeolco model C-60-H spectrometer with the $\text{Ni}(\text{stein})_2 (\text{Cl}_3\text{CCO}_2)_2$ dissolved in deuterated chloroform. A drawing of the spectra arising from the stilbenediamine phenol protons appears as figure 3. The pattern is indicative of a π -delocalization mechanism. The ratio of areas under the peaks from lower to higher field are 2:1:2. "In general, the broader the peak, the closer the corresponding proton is to the source of unpaired electron spin."¹ Therefore, the broad upfield peak is from the orthoprotons, the sharp middle peak is from the para-proton as seen in the ratio of peak areas, and the downfield peak is from the meta-protons. Here the metal-ligand bonding is essentially sigma but with a dominant π -mechanism on the phenyl group.¹

Equation (1) gives the quantitative relationship between the electron spin-nuclear spin coupling constant and the contact shift. "The isotropic contact shift arises principally from the Fermi contact term which is proportional to the electron density at the nucleus."⁸ These contact shifts for isotropic complexes arise from covalency in the metal ion-ligand bond, for an ionic interaction cannot give rise to the needed electron delocalization onto the ligand which then makes the very large perturbation on the nuclear magnetic moments.⁸

RESULTS: for the phenyl protons of $[Ni^{+2}(steln)_2(trichloroacetate)_2]^{-}$

MAGNETIC RESONANCE RESULTS

CONTACT SHIFTS^(a) for the hydrogens on the phenyl groups

o m p of the stilbenediamines.

$$\Delta\nu = 146 \quad -43 \quad 82$$

$$\Delta\nu = 148 \quad -43 \quad 81 \text{ (literature)}^1$$

(a) In Hertz relative to the free ligands

The general quantitative relationship between the electron spin-nuclear spin coupling constant and the contact shift is given by

$$(1) \quad \frac{\Delta\nu}{\nu} = \frac{-4A_n}{g_n} \frac{\chi_e}{\chi_n} \frac{Q(1+I)S(S+1)}{kT}$$

where

A_n = coupling constant between electron spin of Ni^{+2} and nucleus spin of the proton on the phenyl groups.

$g = 2.85$ for Ni^{+2}

$\Delta\nu$ = nmr shift in Hertz

ν = resonance frequency = $60MH_z$

Q = Bohr magneton = 9.272×10^{-21} erg/gauss

k = Boltzmann constant = 1.38045×10^{-16} erg/deg.

T = temperature in K = 295 deg.

SS = total electron spin = 1

I = proton spin = $\frac{1}{2}$

$$\frac{\chi_e}{\chi_n} = 6.577 \times 10^2$$

$$\frac{\Delta\nu}{\nu} = -2.85 \times 10^{-4} A_n \text{ gauss}^{-1}$$

$$A_n = \frac{\Delta\nu}{\nu} \frac{1}{-2.85} \times 10^4 \text{ gauss}$$

$$A_n(\text{ortho}) = \frac{-146 \times 10^4 \text{ gauss}}{(60 \times 10^6) (2.85)} = -.855 \times 10^{-2} \text{ gauss}$$

$$A_{n(\text{meta})} = \frac{43 \times 10^4 \text{ gauss}}{(60 \times 10^6)(2.85)} = .251 \times 10^{-2} \text{ gauss}$$

$$A_{n(\text{para})} = \frac{-82 \times 10^4 \text{ gauss}}{(60 \times 10^6)(2.85)} = -.480 \times 10^{-2} \text{ gauss}$$

Figure 1.

Correlation Diagram for the Triplet States of a d^8 Configuration. The subscript g has been left off for states in O_h and D_{4h} for clarity in presenting the diagram.

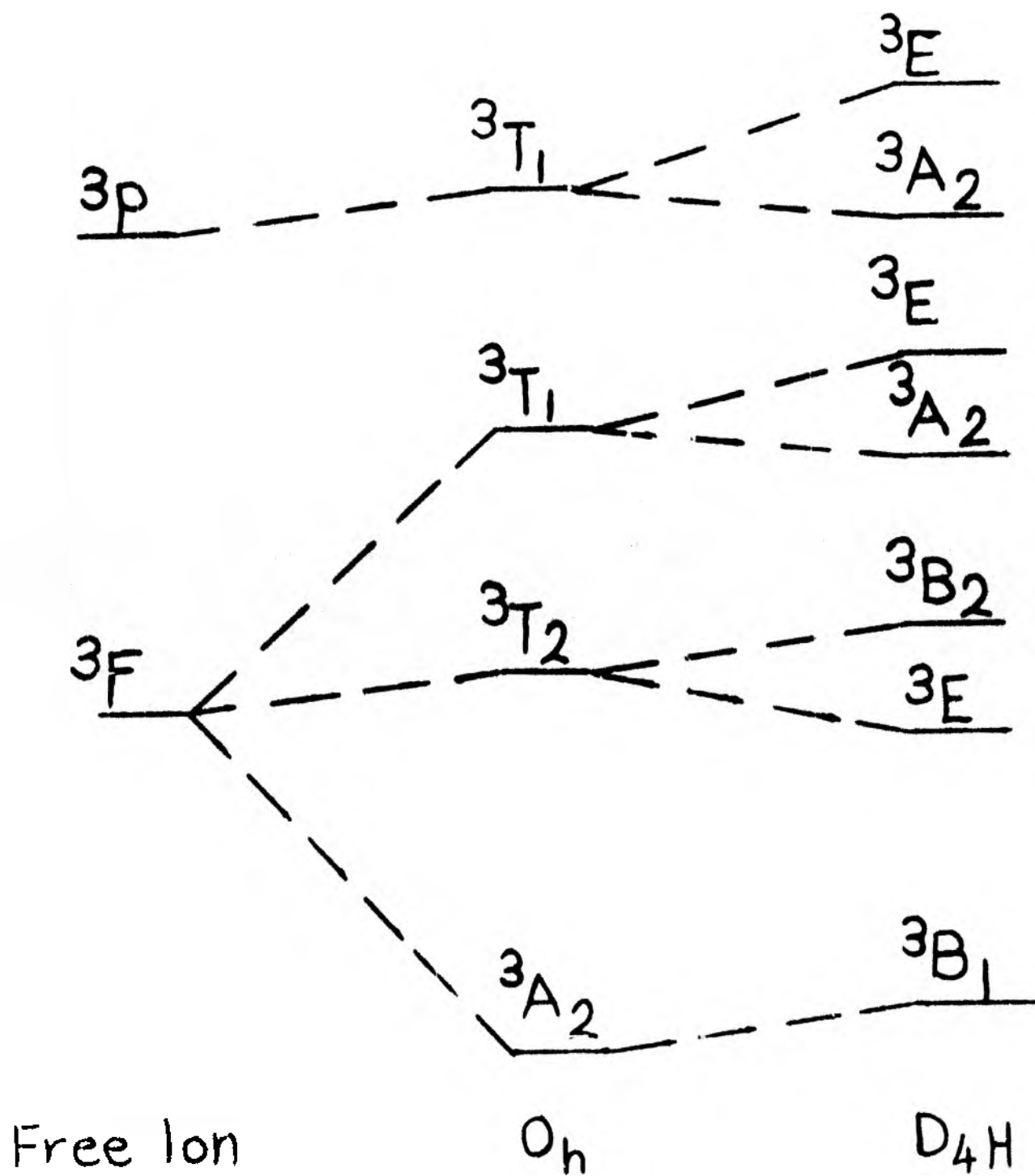


Figure 2. Changes in Metal Ion d-orbital Energies in D_{4h} Symmetry with Axial Ligand Variation.

- Splitting pattern for $Ni(stein)_2(CH_3CO_2)_2$ with the Inductive effect predominating.
- Splitting pattern for $Ni(stein)_2(CCl_3CO_2)_2$.
- Predicted change for $Ni(stein)_2(CH_3CO_2)_2$ with Inductive effect less significant.

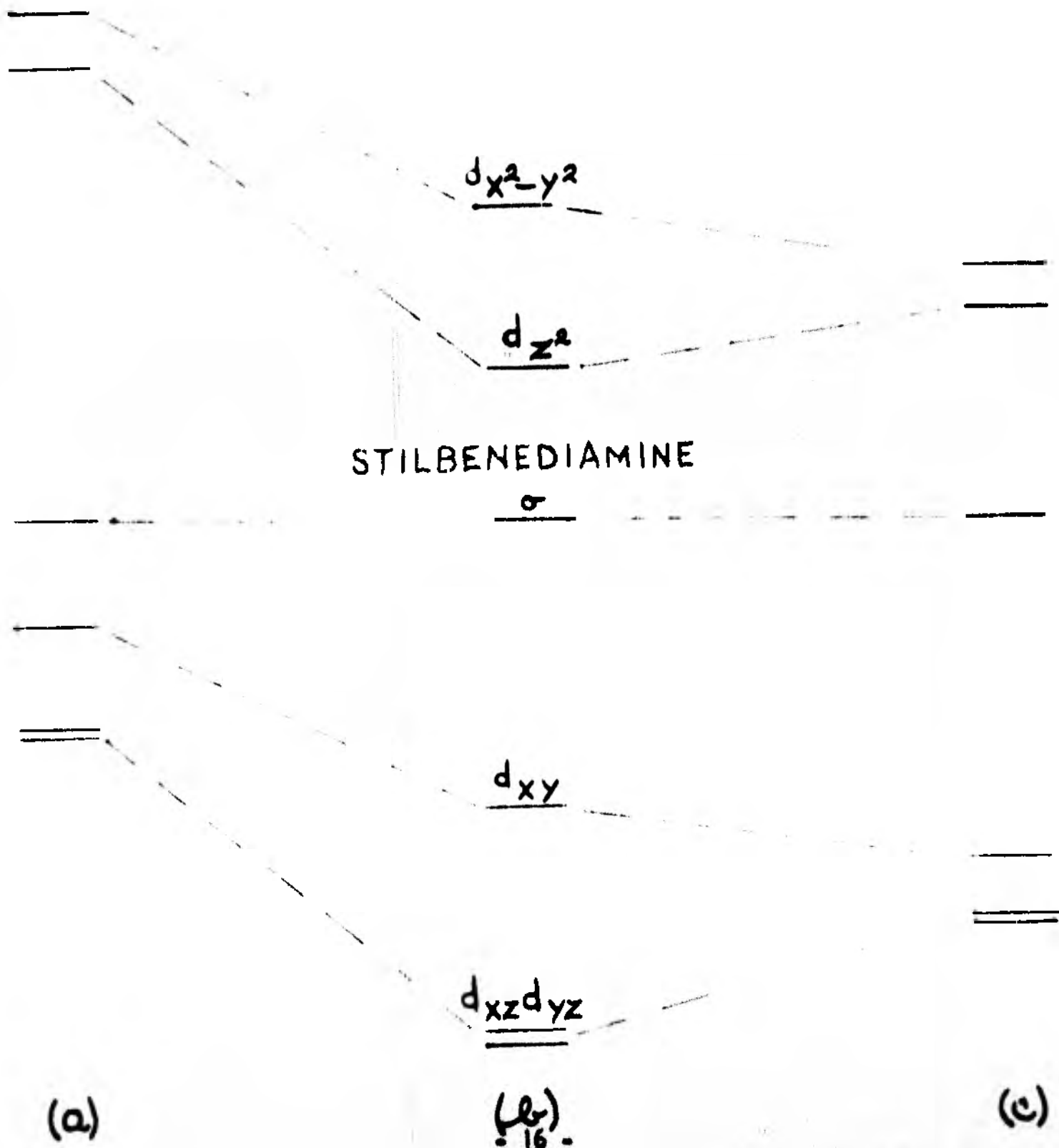


Figure 3.



contact shifts^a

o m p

$\Delta\nu = 146 \quad -43 \quad 82$

^a In Hertz relative to the free ligand

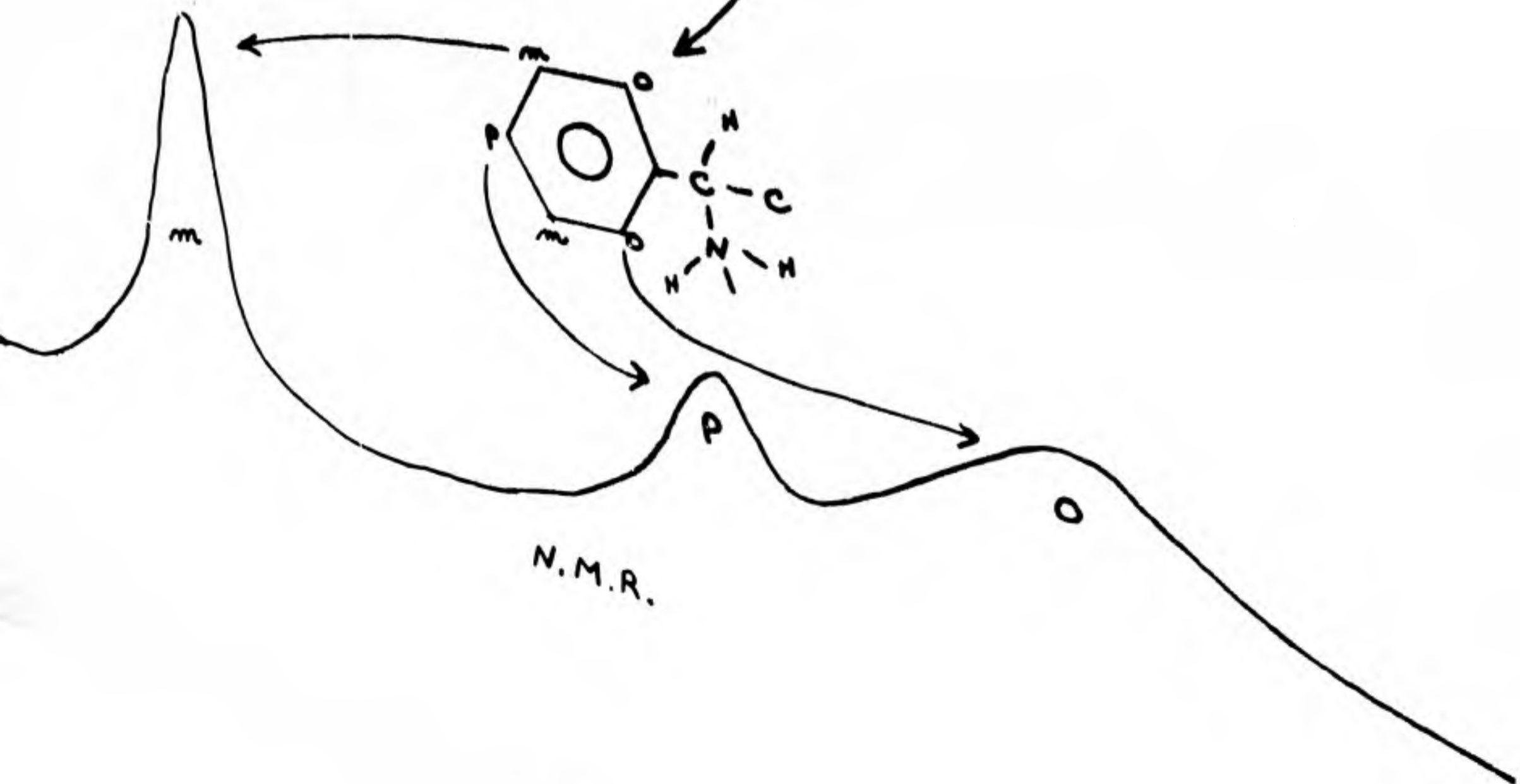
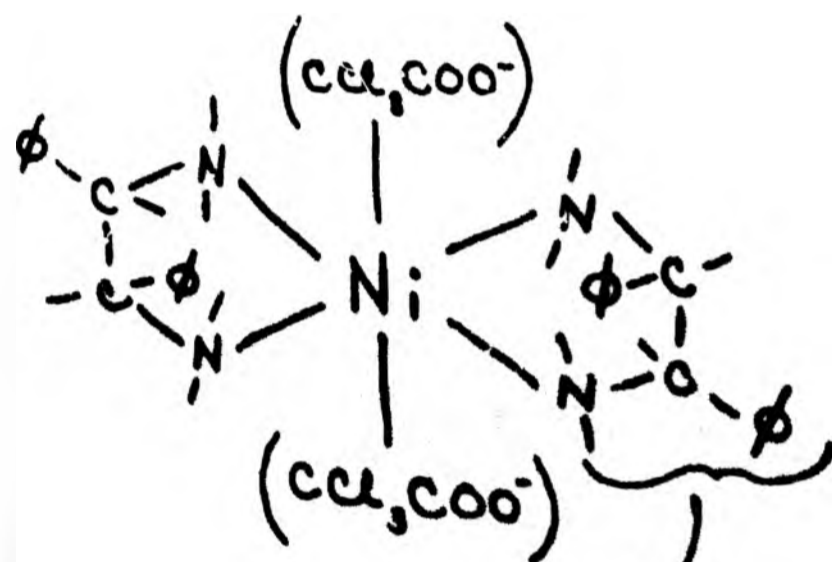


TABLE I

pK Values of Some Substituted Acetates and Benzoates.

acid	pK
acetic	4.75
moniodoacetic	3.12
monochloroacetic	2.85
monobromoacetic	2.67
trichloroacetic	0.70
tribromoacetic	◀ 0.70

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