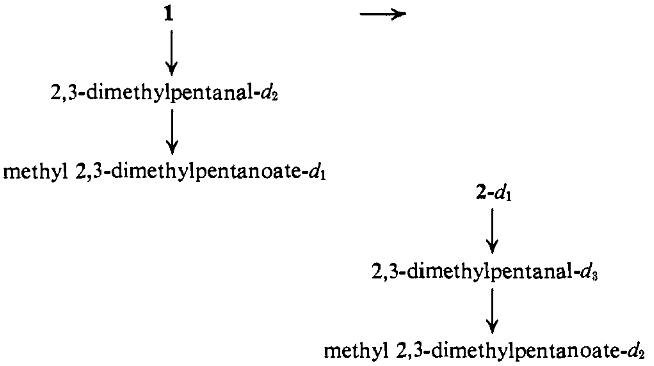
isomerized olefin **2** was substantially monodeuterated (>95%); methyl *threo*-2,3-dimethylpentanoate was more than 90% monodeuterated and the erythro isomer contained two deuterium atoms. Clear evidence was thus provided that **1** and **2** are precursors of individual diastereoisomers, *i.e.*, threo and erythro respectively.



The above results show not only that a cis addition of hydrogen and formyl group occurs in the hydroformylation of both cis and trans internal olefins, but also that the stereospecificity of the reaction is indeed very high. Assuming that the three isomeric aldehydes arise from different intermediates, the stereospecificity of the hydroformylation of the internal double bonds can be considered practically complete.

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Synthesis and Characterization of Novel Pentagonal Bipyramidal Complexes of Iron(II), Cobalt(II), and Zinc(II)

Sir:

We report the synthesis and characterization of the first pentagonal bipyramidal complexes of Fe(II), Co(II), and Zn(II) using the planar pentadentate ligand 2,6-diacetylpyridenebissemicarbazone, DAPSC. Examples of heptacoordination in first-row transition metals are limited, at present, to the heptacyanovanadate ion,[1] $V(CN)_7^{4-}$, to hydrated EDTA complexes of Mn(II)[2] and Fe(III),[3] and a macrocyclic complex of Fe(III).[4] The vanadium complex is the only reported cyanide complex of a first-row transition element with a coordination number greater than six.[5] The flexible nature of EDTA was not expected to produce seven-coordinate molecules routinely. In the case of the macrocycle, the complex was originally postulated as octahedral[6] and apparently was not allowed to react with other metals. However, for a systematic study of seven coordination, it was essential to design a ligand that consistently would produce pentagonal bipyramidal complexes. Therefore, as part of a study of planar pentadentate ligands, we treated an alcohol solution of diacetylpyridine and the appropriate metal chloride with semicarbazide hydrochloride. After slow evaporation of solvent we obtained crystalline products corresponding to the stoichiometry $DAPSC \cdot MCl_2 \cdot 3H_2O$,[7] where M is Fe, Co, Ni, or Zn, which suggested a pentagonal bipyramidal metal complex.[8] The unusual nature of this type of coordination for first-row transition elements prompted an X-ray crystal structure study of these complexes, which has confirmed that they are indeed heptacoordinate.

The Fe(II), Co(II), and Zn(II) complexes are isomorphous. The crystals are monoclinic with cell dimensions of a = 18.096, 17.968, 18.038 Å; b = 13.11, 13.139, 13.112 Å; c = 8.061, 8.052, 8.066 Å; and β = 99.76, 99.86, 100.28° for the Fe(II), Co(II), and Zn(II) complexes, respectively. The densities calculated for four molecules of $DAPSC \cdot MCl_2 \cdot 3H_2O$ per unit cell are 1.615, 1.636, and 1.655 g cm^{-3} compared with 1.62, 1.63, and 1.63 g cm^{-3} found by flotation for the Fe, Co, and Zn complexes. The systematic extinction suggested that the space group was either Ia or $I2/a$ (nonstandard setting of Cc or $C2/c$), with the former being favored by the intensity statistics. The successful analysis carried out in Ia confirmed this choice.

Intensity data for all three complexes were measured using a Syntex $P\bar{1}$ diffractometer with a variable speed θ–2θ scan technique. The data for Fe(II) and Co(II) complexes were obtained using graphite monochromatized Mo Kα radiation but the Zn(II) data were obtained with Ni-filtered Cu Kα radiation. The Zn(II) complex was solved by the heavy-atom technique, with subsequent Fourier syntheses to determine the light atom positions. All electron density maps suggested that the two axial ligands were not both chlorine atoms as would be required in space group $I2/a$ with four molecules per unit cell. The refinement was by least-squares techniques to a final R of 0.059 for the 1172 observed reflections used in the analysis. The Fe(II) and Co(II) complexes were found to be isomorphous, and least-squares refinement used the Zn(II) coordinates as a starting point. The final R values were 0.040 for 1504 observed reflections for the Fe(II) complex and 0.039 for 1518 observed reflections for the Co(II) case.

The pentagonal bipyramidal nature of these complexes is easily seen in Figure 1, which is an ORTEP drawing obtained using the parameters from the Co(II) complex. The five donor atoms N1, N2, N5, O1, and O2 form an approximately planar pentagon around the metal ion, with a chlorine atom and a water molecule in the axial positions. The deviations of the five donor atoms from planarity are identical in the three complexes. If N1 is considered to be on the plane, N2 is above and N5 below the plane by about 0.07 Å and O1 is below and O2 is above the plane by about 0.01 Å. The nature of these distortions is not understood since uncomplexed semicarbazones also show slight deviations from planarity.[9]

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(1) R. L. R. Towns and R. A. Levenson, *J. Amer. Chem. Soc.*, **94**, 4345 (1972).

(2) S. Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, **3**, 27 (1964).

(3) M. D. Lind, M. J. Hamor, T. A. Hamor, and J. L. Hoard, *Inorg. Chem.*, **3**, 34 (1964).

(4) E. Fleischer and S. Hawkinson, *J. Amer. Chem. Soc.*, **89**, 720 (1967).

(5) B. M. Chadwick and A. G. Sharpe, *Advan. Inorg. Chem. Radiochem.*, **8**, 830 (1966).

(6) J. D. Curry and D. H. Busch, *J. Amer. Chem. Soc.*, **86**, 592 (1964).

(7) The chemical analyses were in good agreement with this formulation which was further confirmed by the X-ray studies.

(8) The case of Cu(II) is more complex with two different products resulting from the reaction. These studies are being pursued in more detail.

(9) D. V. Naik and G. J. Palenik, unpublished results.

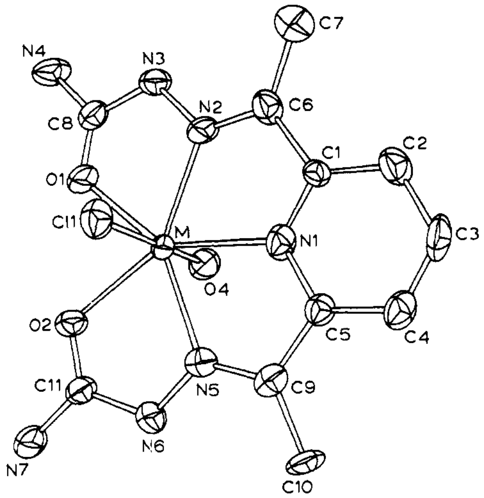

Figure 1. An ORTEP drawing of the chloroaqua(2,6-diacetylpyridinebissemicarbazone)metal(II) cation, where the metal is Fe(II), Co(II), and Zn(II). The atoms N1, N2, N5, O1, and O2 form an approximately planar pentagonal arrangement around the metal ion with Cl1 and O4 in the axial positions. The angles in the Co(II) complexes are N1–Co–N2, 70.3°; N1–Co–N5, 70.4°; N2–Co–O1, 71.9°; N5–Co–O2, 71.4°; and O1–Co–O2, 76.4° (all ±0.2°) and illustrate the approximately planar pentagonal coordination about the Co(II) atom.

The axial metal–chlorine bonds of 2.506, 2.479, and 2.433 Å and the metal–water bonds of 2.153, 2.141, and 2.121 Å, for the Fe, Co, and Zn cases, respectively, both decrease going from Fe to Zn. This change is opposite to that expected on electronic grounds or on the basis of the radius of the metal ion. However, all the in-plane distances are larger in the Zn complex compared with the Fe complex, which suggests that the axial M–Cl and M–OH_2 distances are determined by nonbonded contacts. The importance of intramolecular contacts in copper chloride[10] and gallium chloride[11] complexes has also been noted.

An important conclusion which can be drawn from our studies concerns the possibility of utilizing planar pentadentate ligands to explore pentagonal bipyramidal coordination in other elements. Planar pentadentate ligands have been ignored, apparently, because the pentagonal bipyramidal geometry is relatively rare in coordination complexes. Our results suggest that DAPSC or other planar pentadentate ligands can produce pentagonal bipyramidal complexes in other elements and that the possibilities are virtually limitless. Other studies along these lines are in progress. Finally, as has been demonstrated in other cases,[12] the final stereochemistry of a metal complex appears to be determined by the constraints on the ligand, and unusual geometries may be limited mainly by synthetic difficulties.[13]

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(10) M. Mathew and G. J. Palenik, *Inorg. Chim. Acta*, **5**, 573 (1971).

(11) K. Dymock and G. J. Palenik, unpublished results.

(12) (a) E. Larsen, G. N. LaMar, B. E. Wagner, J. E. Parks, and R. H. Holm, *Inorg. Chem.*, **11**, 2652 (1972); (b) S. C. Jackels and N. J. Rose, *ibid.*, **12**, 1232 (1973).

(13) R. A. D. Wentworth, *Coord. Chem. Rev.*, **9**, 171 (1973) has reviewed this point with respect to the problem of trigonal prismatic *vs.* octahedral coordination.

Stereochemical Dependence of Lone Pair Interactions in the Photoelectron Spectra of Nitrogen–Phosphorus Compounds

Sir:

The discovery[1] of a planar nitrogen geometry in $(CH_3)_2NPF_2$ prompted a surge of interest in the structures[2] and stereochemistry[3] of aminophosphines. The stereochemistry of the corresponding aminophosphoranes has also received attention;[4] however, no structural data have been published for this class of compounds.

The purpose of the present communication is to report studies of the pes (photoelectron spectra) of various nitrogen–phosphorus compounds that suggest interesting conclusions concerning their structures and the effects of lone pair interactions in them.

The monoamines **1** and **4** exhibit single pes peaks at 10.35 and 9.58 eV, respectively (Table I). These peaks can be assigned unambiguously to ionization of the N(2p) lone pair electrons, both on the basis of their line

Table I. Pes Ionization Potentials[a] for N(2p) and P(3p) Lone Pair Orbitals in Nitrogen–Phosphorus Compounds

Compound	No.	N(2p)	P(3p)
$(CH_3)_2NPF_4$	**1**	10.35	
$[(CH_3)_2N]_2PF_3$	**2**	8.84, 9.95	
$[(CH_3)_2N]_3PF_2$	**3**	8.04, 9.03, 9.31	
$(CH_3)_2NPF_2$	**4**	9.58	10.48
$[(CH_3)_2N]_2PF$	**5**	8.18, 9.14	10.40
$[(CH_3)_2N]_3P$	**6**	7.61, 7.89, 8.86	9.98

[a] Vertical ionization potentials in electron volts.

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(1) E. D. Morris and C. E. Nordman, *Inorg. Chem.*, **8**, 1673 (1969).

(2) (a) L. V. Vilkov, L. S. Khaikin, and V. V. Evdokimov, *Zh. Strukt. Khim.*, **10**, 1101 (1969); (b) G. C. Holywell, D. W. K. Rankin, B. Beagley, and J. M. Freeman, *J. Chem. Soc. A*, 785 (1971); (c) A. H. Brittain, J. E. Smith, P. L. Lee, K. Cohn, and R. H. Schwendeman, *J. Amer. Chem. Soc.*, **93**, 6772 (1971); (d) J. R. Durig and J. M. Casper, *J. Cryst. Mol. Struct.*, **2**, 1 (1972); (e) P. Forti, D. Damiami, and P. G. Favero, *J. Amer. Chem. Soc.*, **95**, 756 (1973).

(3) M. P. Simmonin, J. J. Basselier, and C. Charrier, *Bull. Soc. Chim. Fr.*, 3544 (1967); A. H. Cowley, M. J. S. Dewar, and W. R. Jackson, *J. Amer. Chem. Soc.*, **90**, 4185 (1968); D. Imbery and H. Friebolin, *Z. Naturforsch. B*, 236, 759 (1968); H. Goldwhite and D. G. Rowsell, *Chem. Commun.*, 713 (1969); A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, **92**, 1085, 5206 (1970); M. P. Simmonin, C. Charrier, and R. Burgada, *Org. Magn. Resonance*, **4**, 113 (1972); M. P. Simmonin, R. M. Lequan, and F. W. Wehrli, *J. Chem. Soc., Chem. Commun.*, 1204 (1972); I. G. Czismadia, L. M. Tel, A. H. Cowley, M. W. Taylor, and S. Wolfe, *ibid.*, 1147 (1972); S. DiStefano, H. Goldwhite, and E. Mazzola, *Org. Magn. Resonance*, in press.

(4) (a) M. A. Landau, V. V. Sheluchenko, G. I. Drozd, S. S. Dubov, and S. Z. Ivin, *Zh. Strukt. Khim.*, **8**, 1097 (1967); (b) V. V. Sheluchenko, M. A. Sokalskii, M. A. Landau, G. I. Drozd, and S. S. Dubov, *ibid.*, **10**, 142 (1969); (c) M. A. Sokalskii, G. I. Drozd, M. A. Landau, and S. S. Dubov, *ibid.*, **10**, 1113 (1969); (d) J. S. Harman and D. W. A. Sharp, *Inorg. Chem.*, **10**, 1538 (1971); (e) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964); (f) F. N. Tebbe and E. L. Muetterties, *ibid.*, 7, 172 (1968); (g) E. L. Muetterties, P. Meakin, and R. Hoffmann, *J. Amer. Chem. Soc.*, **94**, 5674 (1972); (h) A. H. Cowley and J. R. Schweiger, *J. Chem. Soc., Chem. Commun.*, 560 (1972).