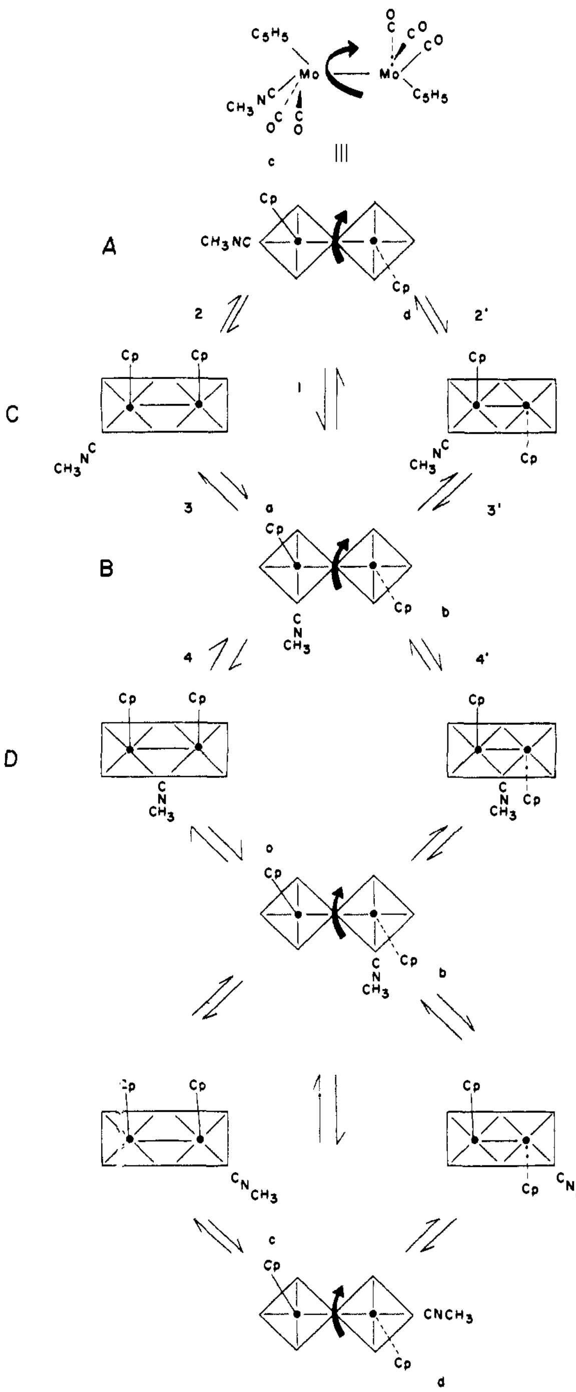
Scheme I

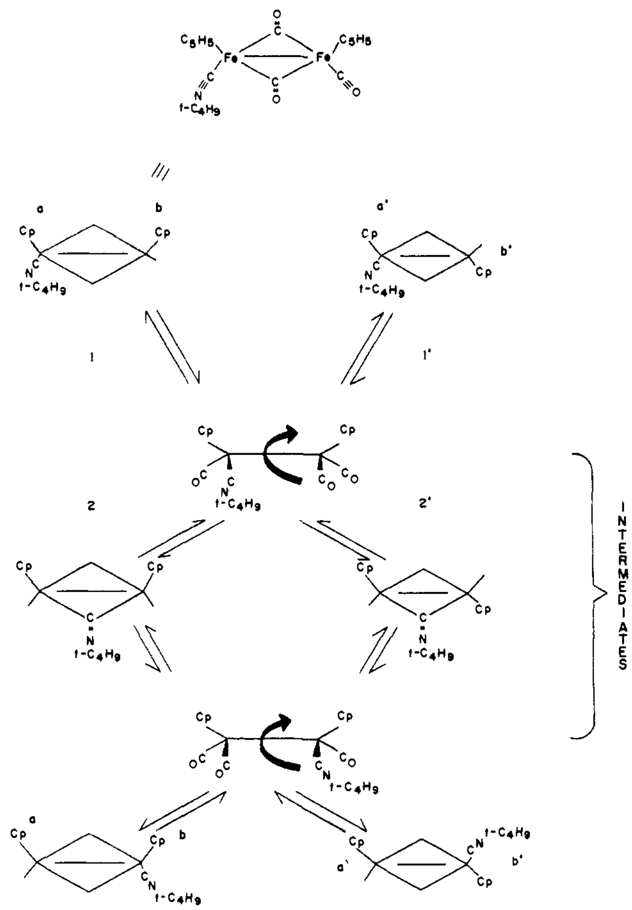


collapses on cooling and re-forms as two sharp singlets of equal intensity at −44°. The *tert*-butyl resonance is single at all temperatures but noticeably broadened at −129°.

This clearly demonstrates a dynamic rearrangement which exchanges the isonitrile ligand between the iron atoms. Scheme II shows the most plausible pathways for this exchange. Rearrangements 1 and 2 together are necessary for transposition of the isonitrile. We resolved two broad terminal isonitrile ir absorptions at 2060 and 2100 cm^{-1}. These can be attributed to two isomers which can interconvert by rearrangements 1. Broadening of the *tert*-butyl resonance at −129° may result from slowing this interconversion.

The observation that isonitrile ligands exhibit the same bifunctional bridge–terminal behavior of carbonyls is significant, since changes in the nitrogen substituent may allow deliberate and useful changes in the bridge–terminal tendency.[5,7,8]

Scheme II



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(5) In the solid state $[(h^5\text{-}C_5H_5)Fe(CO)_2\text{–}Fe(CO)(CN\text{-}t\text{-}C_4H_9)(h^5\text{-}C_5H_5)]$ has a terminal isonitrile, but in $[(h^5\text{-}C_5H_5)Fe(CO)_2\text{–}Fe(CO)(CNC_6H_5)(h^5\text{-}C_5H_5)]$ the isonitrile is bridging.[6]

(6) K. K. Joshi, O. S. Mills, P. L. Pauson, B. W. Shaw, and W. H. Stubbs, *Chem. Commun.*, 181 (1965).

(7) Much of this work was done in the Department of Chemistry, MIT, Cambridge, Mass.

(8) This work was supported in part by the National Science Foundation.

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Received May 17, 1972

Structural Isomerization and Rapid Interconversion of Two Five-Coordinate Cobalt(II) Complexes Containing Chelating Diphosphine Ligands

Sir:

Several new complexes of empirical composition Co(dpe)$_2$SnX$_4$ (dpe = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$; X = Cl, Br, and I) have been isolated from nonaqueous solutions containing a mixture of a cobalt(II) halide, the corresponding stannous halide, and the diphosphine ligand.[1] For the bromide and chloride cases, either a deep red or a deep green crystalline material of identical composition can be isolated depending on the solvent, temperature, and isolation procedures.

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(1) J. K. Stalick, G. Dyer, C. A. McAuliffe, and D. W. Meek, unpublished results.

Table I. Selected Interatomic Distances (Å) and Bond Angles (deg) for $[Co(dpe)_2Cl]SnCl_3$ (**1**) and $[Co(dpe)_2Cl]SnCl_3 \cdot C_6H_5Cl$ (**2**)

Atoms	Distance		Atoms	Angle	
	1	**2**		**1**	**2**
Co–Cl	2.398 (2)	2.251 (5)	Cl–Co–P(1)	94.47 (7)	126.1 (2)
Co–P(1)	2.291 (2)	2.258 (5)	Cl–Co–P(2)	93.96 (7)	92.1 (2)
Co–P(2)	2.254 (2)	2.252 (5)	Cl–Co–P(3)	90.04 (7)	128.1 (2)
Co–P(3)	2.283 (2)	2.268 (5)	Cl–Co–P(4)	95.85 (7)	91.7 (2)
Co–P(4)	2.274 (2)	2.253 (6)	P(1)–Co–P(2)	82.77 (7)	81.0 (2)
			P(1)–Co–P(3)	175.33 (9)	105.7 (2)
			P(1)–Co–P(4)	96.58 (7)	97.1 (2)
			P(2)–Co–P(3)	98.16 (8)	96.2 (2)
			P(2)–Co–P(4)	170.19 (7)	176.2 (2)
			P(3)–Co–P(4)	81.71 (7)	81.2 (2)

The analytical, conductance, magnetic, and electronic spectral data indicate that both the red and green series are low-spin, five-coordinate cobalt(II) complexes. The magnetic moments (μ_{eff} = 2.03–2.14 BM) of the red series are somewhat higher than those of the green series (μ_{eff} = 1.89–1.97 BM). However, both ranges are consistent with the values reported previously for five-coordinate cobalt(II) complexes.[2,3] The electronic spectra of the corresponding red and green complexes in the solid state give the same number of absorption peaks at similar positions. The only significant difference in the spectra of the two series is the greater relative intensity in the bands at ~15,000 cm^{-1} for the green isomer. Both the red and green forms of these complexes convert rapidly (immediately on dissolving) to an equilibrium mixture (predominantly the green form) in all common organic solvents. Three logical possibilities could be proposed to account for the difference in the magnetic and spectral properties of the crystalline compounds: (1) coordination isomerization, *e.g.*, $[Co(dpe)_2X]SnX_3$ and $[Co(dpe)_2SnX_3]X$, (2) bridging halide ligands in the solid state, or (3) different structures for the five-coordinate cations. The ^{119m}Sn Mössbauer spectra helped eliminate the possibilities of coordination isomerization and bridging halides;[4] consequently, the X-ray crystal structures of red $[Co(dpe)_2Cl]SnCl_3$ (**1**) and green $[Co(dpe)_2Cl]SnCl_3 \cdot C_6H_5Cl$ (**2**) were determined.

The red complex **1** crystallized from boiling 1-butanol in space group C_{2h}^5-$P2_1/c$ of the monoclinic system, with four molecules in a unit cell of dimensions a = 17.727 (7), b = 16.431 (6), c = 19.741 (8) Å; β = 122.128 (11)° (t = 23°). The green compound **2** crystallized from an ethanol–chlorobenzene mixture in space group C_i^1-$P\bar{1}$ of the triclinic system, with two molecules of complex and two molecules of chlorobenzene in a unit cell of dimensions a = 11.781 (11), b = 12.846 (12), c = 19.893 (19) Å; α = 106.38 (1), β = 93.76 (2), γ = 101.81 (2)° (t = 24°). Both structures have been solved by heavy-atom methods from three-dimensional X-ray data collected by counter methods. The structure of **1** has been refined to a conventional R factor of 0.065 based on the 5706 reflections for which $F_o^2 > 3\sigma(F_o^2)$, while the structure of **2** has been refined to a conventional R factor of 0.101 using 3484 reflections. The structure parameters for **2** are not as accurate as those for **1** owing to partial anisotropic decomposition of **2** during data collection (standards decreased from 0 to 25%) and some disordering of the chlorobenzene molecules. However, a final difference map showed little residual electron density in the vicinity of the cation (<1.0 e/Å^3); thus the $[Co(dpe)_2Cl]^+$ structure is reasonably well defined.[5]

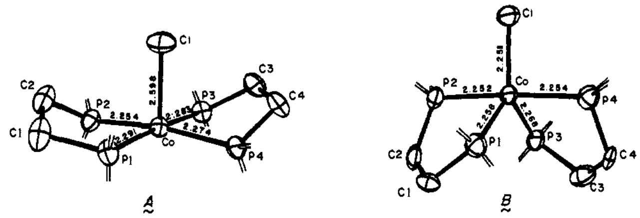

Figure 1. Perspective drawings of the two $[Co(dpe)_2Cl]^+$ cations. Phenyl rings have been omitted for the sake of clarity: A, $[Co(dpe)_2Cl]SnCl_3$ (**1**), red form; B, $[Co(dpe)_2Cl]SnCl_3 \cdot C_6H_5Cl$ (**2**), green form.

Both complexes have discrete, well-separated $[Co(dpe)_2Cl]^+$ cations and pyramidal $SnCl_3^-$ anions in the unit cell; **2** also has a molecule of chlorobenzene which is not associated with either cation or anion. The difference in color between **1** (red) and **2** (green) can be ascribed to a difference in the stereochemistry of the cation. **1** is a square pyramid with an apical Cl atom (Figure 1A), whereas **2** is based on the trigonal-bipyramidal geometry with two P atoms at the axial positions and two P atoms and one Cl atom in the equatorial plane (Figure 1B). The important bond distances and angles for the inner coordination sphere of the two cations are given in Table I. The Co–Cl distance of 2.398 (2) Å at the apex of the square pyramid is longer than the Co–Cl distance of 2.251 (3) Å in the trigonal bipyramid, as expected.[6] Angular distortions from the two idealized five-coordinate geometries result primarily from the 81–83° bite of the diphosphine ligand.

The rapid interconversion red $\rightleftarrows$ green (square pyramid $\rightleftarrows$ trigonal bipyramid) could occur either by a mechanism involving internal reorganization of bonds, *e.g.*, analogous to conformational changes in a cyclopentane ring, or by the dissociation of one end of a chelating ligand followed by the formation of either the square-pyramidal or trigonal-bipyramidal cation. We favor the latter interpretation, as inspection of molec-

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(2) G. Dyer and D. W. Meek, *J. Amer. Chem. Soc.*, **89**, 3983 (1967).

(3) L. Sacconi, *J. Chem. Soc. A*, 248 (1970).

(4) J. K. Stalick, D. W. Meek, B. Y. K. Ho, and J. J. Zuckerman, *Chem. Commun.*, 630 (1972).

(5) A table of the final values of $|F_o|$ and $|F_c|$ (in electrons) for **1** and **2** will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to code number JACS-72-6194. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(6) D. W. Meek and J. A. Ibers, *Inorg. Chem.*, **8**, 1915 (1969).

ular models based on the X-ray results indicates considerable steric hindrance to reorganization. As can be seen from Figure 1, in the square pyramid (**1**) the diphosphine ethylene bridges are directed toward the Co–Cl bond, whereas they are directed away from this bond in the trigonal bipyramid (**2**). Reorganization of **1** to **2** would involve large conformational changes in the ethylene bridge, with concomitant interactions of the phenyl rings.

In addition to being the first accurate X-ray structure determinations on the two limiting stereochemistries for five-coordinate cobalt(II) containing the same set of donor atoms, these two structures demonstrate that one must be very cautious in using electronic spectra to distinguish between square-pyramidal and trigonal-bipyramidal Co(II) complexes. Unless one were fortunate enough to isolate both the trigonal-bipyramidal and the square-pyramidal forms of a five-coordinate cobalt(II) system, it would be very difficult to evaluate definitively the relative intensity of the electronic absorptions in the $\sim$15,000-cm^{-1} region and to assign a structure to the five-coordinate complex. Optical spectra of single crystals of **1** and **2** will be examined to provide definitive assignments for the electronic transitions.

Acknowledgments. The authors are grateful for the financial support of the National Science Foundation and for The Ohio State University Postdoctoral Fellowship (6 months) to J. K. S.

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Received May 25, 1972

Amide–Water Hydrogen Bonding

Sir:

Hydrogen bonding involving the amide linkage in proteins is clearly the most important feature of secondary (α-helical and β-sheet) structure.[1] Thus, it is of great interest to estimate the relative energies of peptide (C=O···H–N) hydrogen bonds and those involving water as a proton donor (O—H···O=C) or proton acceptor (N—H···O) to a peptide group. Several experimental studies[2,3] disagree somewhat on the comparative strength of amide H bonds and amide–H_2O H bonds so one would like to get an independent estimate of these H-bond strengths. Some progress in getting a theoretical estimate of the strength of the amide bond was made by Dreyfus and Pullman,[4] who computed the dimerization energy for a linear $H_2NCHO\cdots H\text{–}NHCHO$ association of two formamides.

In this note, we report *ab initio* molecular orbital calculations (using an STO-3G basis[5]) on the linear formamide dimer $(H_2NCHO)_2$, two formamide–water dimers $[(H_2NCCH){=}O\cdots HOH$ and $CHONH_2\cdots OH_2]$, formaldehyde–water $(H_2CO\cdots HOH)$, ammonia–water $(NH_3\cdots OH_2)$, and the water dimer. Using these results, we address ourselves to the following questions. (1) How competitive is a water molecule for an H-bonding site on a protein (N—H···O=C)? (2) How does the carbonyl of formamide compare with that of formaldehyde in base strength? (3) How much better a proton donor than NH_3 is the NH_2 group in formamide? (4) How do these STO-3G computed dimerization energies compare with those calculated with an STO basis $[(H_2O)_2$ and $H_2CO\cdots HOH]$,[6] with an STO-4G basis $(H_2O)_2$,[7] with an LCAO-double ζ basis $[(H_2O)_2$[8] and $NH_3\cdots OH_2$[9]], and with a very extensive basis $(H_2O)_2$?[10] Answering this last question should give us an estimate of the reliability of the STGO-3 basis to predict dimerization energies.

The minimum energy geometries, computed dimerization energies, and Mulliken populations for the dimers are presented in Table I. It is clear that dimerization energies found using this STO-3G basis are essentially identical with those found using STO,[6] STO-4G,[7] and other[4] small contracted *ab initio* bases. A comparison with more exact calculations for water dimer[10] indicates that our calculated dimerization energies are probably $\sim$2 kcal/mol too high, although dispersion and zero point energy corrections[10] added to an exact SCF calculation might make our agreement with experiment slightly (0.5–1 kcal/mol) better.

We can, however, have confidence in *comparing* different H bonds; the differences in H-bond energy should be more accurate than their absolute value.

In considering our computed H-bond energies, we find that (1) the amide–amide N—H···O=C bond energy is considerably stronger than either amide–water bonds. The amide N–H group appears to be a 3.0 kcal/mol better proton donor than H_2O and the formamide C=O a 2.0 kcal/mol better proton acceptor than water in formamide H bonding. (2) In comparing formamide–water H bonding with formaldehyde–H_2O and ammonia–water, we find the formamide C=O to be a better proton acceptor than the aldehyde C=O by 3.05 kcal/mol and the amide to be a better proton donor than ammonia by 3.1 kcal/mol. (3) These results clearly show that one must apply the concept of "intrinsic" proton donor or acceptor strength with caution. If one extrapolated findings (1) and (2), one would predict that water is a better proton donor than ammonia by 0.1 kcal/mol and water is a better proton acceptor than formaldehyde by 1.05 kcal/mol. A direct comparison using the last three columns of Table I indicates that water is a 2.2 kcal/mol better proton donor than ammonia and a 3.3 kcal/mol better acceptor than formaldehyde.

The population analysis changes presented in Table I follow the trend previously noted for H-bonded systems.[11] In the general H bond A–X···H–Y–B, the A–X molecule transfers some charge to H–Y–B; the X actually gains electrons on H-bond formation (because it pulls more electrons away from A than it gives up) and the proton acceptor atoms (A) *all* lose charge.

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(1) I. D. Kuntz, Jr., *J. Amer. Chem. Soc.*, **94**, 4009 (1972), and references cited therein.

(2) I. M. Klotz and J. S. Franzen, *ibid.*, **84**, 3461 (1962).

(3) J. A. Schellman, *C. R. Trav. Lab. Carlsberg, Ser. Chim.*, **29**, 223 (1955); W. Kauzmann, *Advan. Protein Chem.*, **14**, 1 (1959).

(4) M. Dreyfus and A. Pullman, *Theor. Chim. Acta*, **19**, 20 (1970).

(5) W. I. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1968); standard exponents were used in this calculation.

(6) K. Morokuma, *ibid.*, **55**, 1236 (1971).

(7) J. Del Bene and J. A. Pople, *ibid.*, **52**, 4858 (1970).

(8) P. Kollman and L. C. Allen, *ibid.*, **51**, 3286 (1969).

(9) P. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, **93**, 4991 (1971).

(10) D. Hankins, J. Moscowitz, and F. Stillinger, *J. Chem. Phys.*, **53**, 4544 (1970).

(11) P. Kollman and L. C. Allen, *Chem. Rev.*, 72, 283 (1972).