Table I.[a] Emission Mossbauer Parameters of α- and β-^{57}Co^{II}Pc at 80°K

Polymorph and its source	δ,[b] mm/sec	Δ, mm/sec
(I) α-^{57}CoPc (sulfuric acid precipitation	0.45 ± 0.01	2.50 ± 0.01
(II) α-^{57}CoPc (sublimation)	0.45 ± 0.01	2.54 ± 0.01
(III) β-^{57}CoPc (heating of I)	0.47 ± 0.01	2.70 ± 0.01
(IV) β-^{57}CoPc (sublimation)	0.47 ± 0.01	2.67 ± 0.01

[a] The observed emission line widths are about 0.43 mm/sec as compared to absorber line widths of 0.33 mm/sec. The average values of δ and Δ resulting from several independent experiments are reported here. [b] Isomer shifts are reported with respect to iron.

Table II. Absorption Mossbauer Parameters of α- and β-Fe^{II}Pc at 80°K and Parameters Reported in the Literature without Characterizing the Form

	δ,[a] mm/sec	Δ, mm/sec
α form	0.46 ± 0.01	2.49 ± 0.01
β form	0.48 ± 0.01	2.68 ± 0.01
Hudson and Whitfield[b]	0.51 ± 0.02	2.62 ± 0.02
Taube, *et al.*[c]	0.48 ± 0.01	2.60 ± 0.01
Moss and Robinson[d]	0.53 ± 0.02	2.62 ± 0.02
Dezsi, *et al.*[e]	0.64	2.64
Thompson, *et al.*[f]	0.48	2.63

[a] Isomer shifts are reported with respect to iron. [b] A. Hudson and H. J. Whitfield, *Inorg. Chem.*, **6**, 1120 (1967). [c] R. Taube, H. Drevs, E. Fluck, P. Kuhn, and K. F. Brauch, *Z. Anorg. Allg. Chem.*, **364**, 297 (1969). [d] T. H. Moss and A. B. Robinson, *Inorg. Chem.*, 7, 1692 (1968). [e] I. Dezsi, A. Balazs, B. Molnar, V. D. Gorobchenko, and L. I. Lukashevich, *J. Inorg. Nucl. Chem.*, **31**, 1661 (1969). [f] J. L. Thompson, J. Ching, and E. Y. Fung, *Radiochim. Acta*, **18**, 57 (1972).

understood if we visualize the π electrons of the aromatic rings of the neighboring molecules as being delocalized through the two axially situated nitrogens onto the $3d_{xz}$ and $3d_{yz}$ orbitals of the central iron atom as originally suggested by Heilmeier and Harrison.[17] This would enhance the shielding of the s electrons by the d electrons and thereby decrease the s-electron density on the iron nucleus. Therefore, this can account for the larger chemical shifts observed. The degree of delocalization of electrons in d orbitals required to produce the observed increase can be roughly estimated as 0.02 electron. This estimate is based on the observation that a complete removal of a d electron, as in going from Fe^{2+} to Fe^{3+}, results in a change of about 1 mm/sec in the isomer shift.

Regarding the differences in Δ, the contributions of $3d_{xz,yz}$ orbitals toward the V_{zz} are negative and therefore a slight increase in the electronic density in these orbitals could only lead to a small diminution in the quadrupole splittings of the β forms. However, we observe an enhancement of Δ. It seems that the two axial nitrogens are not situated exactly on the octahedral positions but form a very slightly distorted octahedron. The slightly asymmetrical situation of the nitrogens presumably results in a stronger interaction with one of the $3d_{xy,yz}$ orbitals and thereby lifts the degeneracy of the orbitals. This would lead to a nonzero value for the asymmetry parameter of the field gradient, η. The decrease in quadrupole splitting due to flow of about 0.02 electron in the $3d_{xz,yz}$ can be more than compensated by the increase in Δ arising from the asymmetry parameter η, *i.e.*, $^1/_3(\Sigma\beta f)^2$ in the expression. An orbital occupation of approximately $(3d_{xz})^{1.6}(3d_{yz})^{1.4}$ or *vice versa* for the β forms can account for the experimentally observed increase in quadrupole splitting.

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Registry No. ^{57}Co^{II}Pc, 51271-00-2; Fe^{II}Pc, 132-16-1; ^{57}CoCl$_2$, 16413-89-1; phthalic anhydride, 85-44-9; urea, 57-13-6.

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Cis and Trans Effects on the Proton Magnetic Resonance Spectra of Cobaloximes

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The pmr spectra of cobaloximes LCo(DH)$_2$X, with X = NO$_3$, SeCN, Cl, Br, NCS, N$_3$, SCN, *i*-PrXan, CN, NO$_2$, and CH$_3$, L = 4-*tert*-butylpyridine (*t*-Bu(py)) and tri-*n*-butylphosphine (Bu$_3$P), and DH = monoanion of dimethylglyoxime, are reported. Except for the linear triatomics, which form a bent bond to cobalt (N$_3$, SCN, SeCN), the chemical shifts of the cis dioxime methyl resonance and the trans α H resonance of (*t*-Bu(py))Co(DH)$_2$X are linearly related. The slope of the line is approximately in agreement with the screening formula of an axially anisotropic group with the cobalt at the center. Analysis of the dependence of the chemical shifts on X in (*t*-Bu(py))Co(DH)$_2$X and of the variation of coupling constants in Bu$_3$PCo(DH)$_2$X is consistent with rehybridization of the Co–X bond. Specifically, it is suggested that the degree of 4s character in the Co–X bond increases along the series. According to Ramsey's equation, the paramagnetic contribution perpendicular to the axial direction should decrease. This interpretation differs from a previous study of cobaloximes.[1] It is shown that previous work utilized incorrectly formulated compounds. More specific synthetic procedures are reported, as is the fractional separation of the N- and S-bonded thiocyanate complexes when L = *t*-Bu(py). Evidence is presented for the formation of the transient species (1-MeImd)Co(DH)$_2$(ONO), during the ligand-exchange reaction of (Ph$_3$P)Co(DH)$_2$NO$_2$ with 1-MeImd (1-methylimidazole).

Introduction

A detailed study of the effect of the variation of one ligand on the pmr spectra of other ligands in cobaloxime complexes has been reported.[1] Cobaloximes[2] are complexes containing the moiety Co(DH)$_2$, where DH = monoanion of dimethylglyoxime. The specific cobaloximes studied were reported as being the neutral species LCo(DH)$_2$X, where L = triphenylphosphine (Ph$_3$P) and pyridine (py) and X = NO$_2$, CN, Cl, Br, I, ONO, and alkyls.[1] We felt that this series was worthy of extension and reinvestigation for several reasons, which are outlined below.

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(1) H. A. O. Hill and K. G. Morallee, *J. Chem. Soc. A*, 554 (1969).

(2) G. N. Schrauzer, *Accounts Chem. Res.*, 1, 97 (1968).

There is mounting evidence that the chemistry of cobaloxime (as well as other B_{12} models) and of platinum(II) complexes are related.[3] The chemistry of Pt(II) complexes is unparalleled among transition metals in the extent of investigations into the dependence of chemical and spectral properties of one ligand on the nature of the other coordinated ligands.[4] From such extensive studies, a rather coherent picture has emerged.[4] One could anticipate applying this understanding to cobaloxime complexes.

There have been many investigations into the factors which influence the bonding of thiocyanate in second- and third-row transition metals, including platinum(II).[5] Cobaloxime thiocyanate complexes have served to provide comparable data for a first-row transition metal.[6] It was hoped that some new information about thiocyanate bonding might be derived from a pmr study of cobaloximes which included both S- and N-bonded thiocyanate.

The most important property of cobaloximes is the ability to form very stable Co–C bonds.[2] Considerable ambiguity exists as to the nature of this bond ($Co^{III}CH_3^-$, $Co^{II}CH_3$, or $Co^{I}CH_3^+$),[7] and an understanding of the factors influencing the chemical shift might aid in the resolution of this ambiguity.

There were other more specific reasons for the reinvestigation. These include several unusual properties of the complexes reported[1] and, particularly, the finding that nitrito complexes were more stable than nitro complexes. Since cobaloximes are usually considered "soft,"[8] this order of stability was puzzling.

The preparation of isomerically pure species was a principal primary objective of this research since in the previous pmr study[1] the preparative procedures led to isomeric mixtures. General methods of synthesis of $LCo(DH)_2X$ complexes have been reported by Schrauzer.[9] We report some observations on the aerial oxidation method of synthesis as well as some improved preparative methods. The details of the synthesis and separation of $(t\text{-Bu(py)})Co(DH)_2CNS$ isomers[10] are also reported (t-Bu(py) = 4-*tert*-butylpyridine and CNS does not imply a bonding mode).

Results

Preparation of Complexes. The usual procedure for syntheses of complexes of the type $LCo(DH)_2X$ involves aerial oxidation of stoichiometric mixtures according to eq 1.

$$2L + 2DH_2 + CoX_2 + {}^1/_4O_2 \rightarrow LCo(DH)_2X + LHX + {}^1/_2H_2O \quad (1)$$

Costa[11] found that the direct oxidation using L = phosphine ligands often led to the salts $[L_2Co(DH)_2][Co(DH)_2X_2]$, when a modification of the synthetic procedure[9] was used. Hill[1] also reported salt formation. In initial preparative studies of $(t\text{-Bu(py)})Co(DH)_2CNS$, aerial oxidation led to $[(t\text{-Bu(py)})_2Co(DH)_2][Co(DH)_2(CNS)_2]$ as the least soluble product as well as a mixture of the more soluble $(t\text{-Bu(py)})Co(DH)_2NCS$ and $(t\text{-Bu(py)})Co(DH)_2SCN$ (in roughly equal proportions). Fractional crystallization of the metal complexes was complicated by the presence of the salt. A more stereoselective route was sought by using thiocyanate substitution of another acido group. However, in our hands the general method of preparation of $LCo(DH)_2X$ compounds often led to the isolation of considerable amounts of $[L_2Co(DH)_2][Co(DH)_2X_2]$. The particular synthesis described in ref 9 is that for $pyCo(DH)_2Cl$, but again we obtained mainly $[(py)_2Co(DH)_2][Co(DH)_2Cl_2]$. Dr. Alan M. Sargeson had the preparation repeated for us in his laboratory, and the material proved to contain 40% $[(py)_2Co(DH)_2][Co(DH)_2Cl_2]$.

The underlying cause of this problem is undoubtedly the occurrence of the equilibrium

$$2LCo(DH)_2X \overset{Co(II)}{\rightleftharpoons} [L_2Co(DH)_2][Co(DH)_2X_2]$$

which is catalyzed by the cobalt(II) present before oxidation is complete. The variability in the purity of the reagents will influence the residual cobalt(II) concentration and thereby the rapidity of attainment of equilibrium. The position of the equilibrium will depend on the polarity of the solvents as well as the nature of L and X. For example, if the filtrate from the preparation of $(Ph_3P)Co(DH)_2Cl$[9] is worked up without delay, the isolated product contains the salt. However, if the filtrate is allowed to stand in the absence of air, more pure neutral complex crystallizes. The complex $pyCo(DH)_2Cl$ can be converted to the ion $[Co(DH)_2Cl_2]^-$ by dissolving the former in chloroform, adding tetraphenylarsonium chloride, and heating the solution in contact with water. On the other hand, if the oxidizing agent $BrCCl_3$ is also added to the chloroform, no conversion takes place.

Costa[11] has proposed an alternative synthesis for the neutral monomer involving phosphine ligands. The method requires preparing $Co(DH)(DH_2)Cl_2$, conversion into $H_2OCo(DH)_2Cl$, and finally conversion into $LCo(DH)_2X$. A much more convenient method was devised using $Co(DH)(DH_2)Cl_2$ according to eq 2 and 3. These reactions readily yielded $LCo(DH)_2Cl$ for a number of phosphine and amine ligands. Re-

$$2L + Co(DH)(DH_2)Cl_2 \rightarrow LCo(DH)_2Cl + LHCl \quad (2)$$

$$L + Bu_3N + Co(DH)(DH_2)Cl_2 \rightarrow LCo(DH)_2Cl + Bu_3NHCl \quad (3)$$

action 3 serves well either when the salt $LH[Co(DH)_2Cl_2]$ is insoluble or when the ligand is expensive. The neutral species are favored in the low dielectric solvent chloroform and substitution of the halo group, necessitating charge separation, is impaired. The pure $(t\text{-Bu(py)})Co(DH)_2Cl$ produced in this way was readily converted to a mixture of the neutral thiocyanate complexes. The species $Co(DH)(DH_2)Cl$ is a convenient starting material and is formed by mixing $CoCl_2 \cdot 6H_2O$ and dimethylglyoxime in the correct molar ratio in acetone, filtering, and allowing the solution to stand overnight.

Structural Assignments. The favorable hydrogen bond formed between the two dioxime ligands leads to the preferential formation of trans complexes. These complexes containing the moiety $Co^{III}(DH)_2$ normally exhibit coordination or linkage isomerism or the combination of the two types of isomerism. When X = CNS, both types of isomerism were found in this study. In practice, salt formation is easily identified from pmr spectra or by metathesis reactions with

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(3) T. G. Appleton and M. A. Bennett, *J. Organometal. Chem.*, 55, C88 (1973); H. A. O. Hill, K. G. Morallee, F. Cernivez, and G. Pellizer, *J. Amer. Chem. Soc.*, 94, 277 (1972).

(4) T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, 10, 335 (1973).

(5) J. L. Burmeister, *Coord. Chem. Rev.*, 3, 225 (1968); D. W. Meek, P. E. Nicpon, and V. I. Meek, *J. Amer. Chem. Soc.*, 92, 5351 (1970).

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(9) G. N. Schrauzer, *Inorg. Syn.*, 11, 61 (1968).

(10) L. A. Epps and L. G. Marzilli, *J. Chem. Soc., Chem. Commun.*, 109 (1972).

(11) G. Costa, G. Tauzher, and A. Puxeddu, *Inorg. Chim. Acta*, 3, 45 (1969).

large anions or cations such as $As(C_6H_5)_4^+$ and $B(C_6H_5)_4^-$ (see Experimental Section). Linkage isomers are not so readily characterized. Spectroscopic studies on the bonding mode of thiocyanate in (*t*-Bu(py))Co(DH)$_2$CNS complexes and the three isomers of the $[Co(DH)_2(CNS)_2]^-$ anion have been reported.[10,12] The equilibrium distribution of S,S, N,S, and N,N isomers in DMF found for [(*t*-Bu(py))$_2$Co(DH)$_2$][Co(DH)$_2$(CNS)$_2$] was the same as that found for $As(C_6H_5)_4[Co(DH)_2(CNS)_2]$.[12]

In addition to thiocyanate, the ligands CN, NO_3, and NO_2 have various bonding capabilities. We have assumed that the cyano group is bonded *via* carbon. The bonding of the nitro groups is best considered in the section on pmr spectra. The nitrate group offers two concerns. First, the group is quite a weak ligand and may not be coordinated and, second, the group could conceivably be bidentate. Several lines of evidence point to a coordinated nitrate group. The product obtained on reaction of (*t*-Bu(py))Co(DH)$_2$Cl with silver nitrate exhibits two diagnostic bands in the ir spectrum, one at 3400 cm^{-1} indicating water and a sharp band at 1385 cm^{-1} due to ionic nitrate.[13] The material is poorly soluble in organic solvents. Upon drying at 111° for 13 hr under vacuum, these peaks disappear and a strong band appears at 1275 cm^{-1}. In addition other bands appear at 1512, 1504, and 980 cm^{-1}. These four bands are characteristic of coordinated nitrate.[13] This change in ir spectrum is accompanied by a darkening of the sample and a considerable increase in solubility in organic solvents. Without Raman spectra, it is not possible to say whether the nitrate is acting as a unidentate or a bidentate ligand but unidentate coordination seems reasonable.

Pmr Studies. The chemical shifts of the oxime methyl resonances of the triphenylphosphine compounds studied by Hill (using his structural assignment) fall into four groups.[1] In the order of increasing τ values in CH_2Cl_2, these are group I (X = CN, NO_2), group II (halogens), group III (-ONO), and group IV (alkyls). The chemical constitutions of both groups II and IV are well established.[9,11] Compounds of groups I and III were prepared for the pmr study. Difficulties existed in obtaining a pure complex for X = CN without contamination from [(Ph$_3$P)$_2$Co(DH)$_2$][Co(DH)$_2$CN$_2$].[1] Two products were obtained using NaNO$_2$; these were thought to be linkage isomers. Based on the pmr trends of group II and IV compounds and of the impure CN complex, the pmr data were used to assign the structure of the poorly soluble product as the nitro linkage isomer (group I) and the structure of the soluble material as the nitrito isomer (group III).

The results of our pmr study for L = *t*-Bu(py) and Bu$_3$P are given in Table I. For the compounds with X = NO_2, the chemical shift of the oxime methyl resonances corresponds to the group III isomer. For X = CN, the oxime methyl resonance is found at quite a high field. A clear contradiction between our results and those of Hill was evident. Reexamination of Hill's paper revealed several puzzling properties of the nitro (group I) compound. It was poorly soluble for no apparent reason, and also no splitting of the methyl resonances by ^{31}P was observed. Furthermore, the ir bands attributable to the NO_2 group were similar for both group I and group III NO_2 compounds.

Table I. Pmr Data for LCo(DH)$_2$X Complexes[a]

	L = *t*-Bu(py)[b]		L = Bu$_3$P[c]	
X	τ(oxime CH$_3$)	τ(α H)[d]	τ(oxime CH$_3$)	J_{PH}, Hz
NO$_3$	7.62	2.13	7.63	0.8
NCS	7.65	2.03	7.63	1.4
N$_3$	7.66	1.92	7.64	1.4
Br	7.67	2.02	7.66	1.2
Cl	7.67[e]	1.99	7.67	1.3
SCN	7.67	1.91	7.63	1.4
NO$_2$	7.73	1.93	7.66	1.4
i-PrXan[f]	7.76	1.85	7.69	2.0
CN	7.79	1.79	7.71	2.1
CH$_3$	7.93	1.63	7.84	3.3

[a] CH$_2$Cl$_2$, in τ relative to TMS, [Co] = 0.1 *M*. [b] 100 MHz, order the same as found on 60 MHz. [c] 60 MHz, prepared *in situ* from *t*-Bu(py) complexes by addition of phosphine. [d] Other observable protons: *t*-Bu varied from τ 8.73 to 8.80 and β H from τ 2.66 to 2.85. [e] Independent of concentration in range 0.01–0.2 *M*. [f] Isopropyl xanthate.

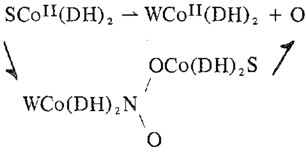
Hill's preparation of the less soluble "(Ph$_3$P)Co(DH)$_2$NO$_2$" isomer was repeated and the material obtained corresponded in its properties with that reported.[1] The more soluble "(Ph$_3$P)Co(DH)$_2$ONO"[1] isomer was also obtained. The ir bands attributable to the NO_2 group (Hill's in parentheses) were as follows: less soluble "nitro," 1406 (1408), 1311 (1310), and 818 (817) cm^{-1}; more soluble "nitrito," 1408 (1410), 1310 (1313), and 811 (806) cm^{-1}. The more soluble isomer had a pmr spectrum which agreed with that reported.[1] The less soluble "nitro" compound had a singlet at τ 7.71 as reported,[1] but the spectrum contained a triplet at τ 8.47. When $As(C_6H_5)_4[Co(DH)_2(NO_2)_2]$ was added to the solution, the peak originally at τ 7.71 increased in size. The pmr spectra clearly indicate that the less soluble product is [(Ph$_3$P)$_2$Co(DH)$_2$][Co(DH)$_2$(NO$_2$)$_2$]. The similarity in the infrared spectra of the two isomers suggests that the NO_2 group is bonded in the same manner in both isomers. Similar ir frequencies have been attributed to N-bonding NO_2 groups by many workers[14] and ^{15}N studies of related dimethylglyoxime complexes have confirmed that these bands are assignable to the NO_2 group.[15] The spectrum of the (*t*-Bu(py))Co(DH)$_2$NO$_2$ complex has bands at 1420, 1315, and 815 cm^{-1}, and N-bonding is also probable in this compound.

Although the experiments outlined in the previous paragraph demonstrate that all the NO_2 compounds are N bonded, we undertook to establish further the instability of the nitrito linkage isomer. We reasoned that electron transfer *via* a nitro bridge should lead to the nitrito isomer. Consider the cobalt(II)-catalyzed ligand-exchange reaction[16]

$$S + WCo^{III}(DH)_2NO_2 \rightarrow SCo^{III}(DH)_2NO_2 + W$$

(where S and W are, respectively, strong and weak ligands in their ability to form stable cobalt(III) complexes). The first step is most likely to be an inner-sphere electron transfer involving remote attack on one of the nitro oxygens (a). We

$$WCo^{III}(DH)_2NO_2 + SCo^{II}(DH)_2 \rightarrow WCo^{II}(DH)_2 + ONOCo^{III}(DH)_2S$$



(a)

were not able to observe the nitrito linkage isomer with W =

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(12) L. A. Epps and L. G. Marzilli, *Inorg. Chem.*, 12, 1514 (1973).

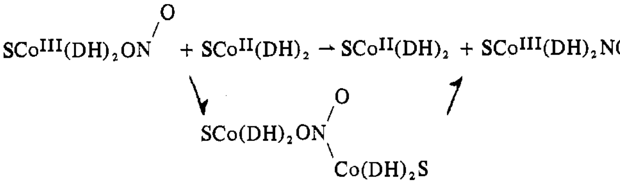
(13) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley-Interscience, New York, N. Y., p 171. The preparation of the nitrato complex is reported elsewhere: W. C. Trogler and L. G. Marzilli, *Inorg. Chem.*, 13, 1008 (1974).

(14) S. G. Clarkson and F. Basolo, *Inorg. Chem.*, 12, 1528 (1973), and references therein.

(15) M. Tamaki, I. Masuda, and K. Shinra, *Bull. Chem. Soc. Jap.*, 45, 171 (1972).

(16) L. G. Marzilli, J. G. Salerno, and L. A. Epps, *Inorg. Chem.*, 11, 2050 (1972).

$(C_6H_5)_3P$ and S = py. Reaction b is probably fast, since attack



$$\mathrm{SCo^{III}(DH)_2ON{=}O + SCo^{II}(DH)_2 \rightarrow SCo^{II}(DH)_2 + SCo^{III}(DH)_2NO_2}$$
$$\searrow \quad \mathrm{SCo(DH)_2ON(O)Co(DH)_2S} \quad \nearrow \qquad \text{(b)}$$

on the softer N by soft $SCo^{II}(DH)_2$ is favorable and because the nitrito isomer is unstable. For the nitrito intermediate to be sufficiently long-lived for observation two conditions must be met. Reaction a must be as rapid as possible (weakest possible W and strongest possible S) and reaction b must be slow. Unfortunately, the rate of reaction b will probably not depend greatly on the nature of S. However, if S were added in *less* than the stoichiometric amount, much of S would be in the form $SCo^{III}(DH)_2ONO$ and the concentration of $SCo^{II}(DH)_2$ would be low (after (a) had progressed sufficiently). Choosing a very poor ligand W would also diminish the reverse of (a), a reaction which provides a source of $SCo^{II}(DH)_2$. The $SCo^{II}(DH)_2$ produced by the reverse of (a) eventually will lead to conversion of all the unstable nitrito product to nitro product. Additionally, the nitrito isomer might be thermally unstable to its linkage isomer.

Spectral changes (pmr) accompanying the reaction of *t*-Bu(py) with $(Ph_3P)Co(DH)_2NO_2$ are consistent with less than 10% formation of (*t*-Bu(py))$Co(DH)_2ONO$. However, the analogous experiment in which 1-methylimidazole (1-MeImd) is substituted for *t*-Bu(py) proved more successful (Figure 1; 1-MeImd is a much better ligand than *t*-Bu(py)[16]). When the first pmr spectrum could be taken after addition of 1-MeImd to $(Ph_3P)Co(DH)_2NO_2$ (1 min), two new oxime methyl peaks were in evidence. The major peak at τ 7.69 diminished with time as the upfield peak at τ 7.73 increased. Eventually, the downfield signal was lost in the noise. These results provide strong evidence for the existence of a nitrito intermediate. Furthermore, our analysis of the effect of X on the chemical shifts of the dioxime methyl resonance (Discussion) leads us to predict that the signal for the nitrito isomer would be downfield from that of the nitro isomer.

Discussion

Nuclear magnetic resonance has been used to assess the interaction of ligands coordinated to the same metal center.[17] Most success is anticipated for nuclei heavier than hydrogen because the chemical shifts of these nuclei are dominated by local paramagnetic shielding. On the other hand, the chemical shift of hydrogen is dependent primarily on local diamagnetic shielding and is influenced by neighboring group anisotropy. Hydrogen nuclei are almost ubiquitous and criteria to assess chemical shift data would therefore be quite useful.

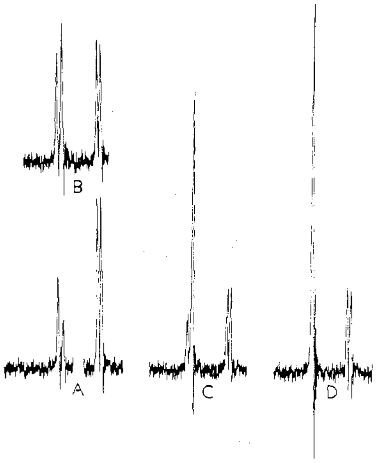


Figure 1. Spectra of oxime methyl pmr signals after addition of 1-MeImd (initially 0.07 *M*) to a 0.1 *M* solution of $(Ph_3P)Co(DH)_2NO_2$ (upfield doublet, τ 8.02; J = 2 Hz due to long-range coupling with phosphorus) in CH_2Cl_2. Downfield peaks at τ 7.69 and 7.73 correspond to (1-MeImd)$Co(DH)_2(ONO)$ and (1-MeImd)$Co(DH)_2(NO_2)$ respectively. Variation of the methyl pmr of coordinated 1-MeImd (not shown) was also consistent with the nitrito and nitro complexes with resonances at τ 6.43 and 6.44, respectively, in the proper ratios: A, 1 min after addition of 1-MeImd; B, 2 min; C, 4 min; D, 10 min.

The two approaches previously used to explain chemical shift data of hydrogen in ligands coordinated to cobalt(III) have employed the local diamagnetic shielding (cobaloximes)[1] and the neighboring group effect of cobalt ($[Co(macrocycle)X_2]^+$ complexes).[18] The basis for using diamagnetic shielding was Hill's observation of a near-perfect correlation of the oxime methyl resonances of $LCo(DH)_2X$ complexes with the σ_{para} functions of X. We have shown that the NO_2 compounds used were wrongly formulated and believe that the CN compound is also incorrect. A least-squares fit of our data for (*t*-Bu(py))$Co(DH)_2X$ (X = Cl, Br, NO_2, CN, CH_3) with σ_{para} functions gives correlation coefficients of 0.78 and 0.38 for the oxime methyl resonance and the α H resonance, respectively. These values represent low confidence limits (for so few data points). A good correlation of chemical shift with the spectrochemical series has been found for the macrocyclic complexes. Such correlations[18] are well founded theoretically[19] and involve mixing a paramagnetic excited state into the ground state. The excited-state energy is a function of the ligand field strength of X, but the d–d bands in the cobaloximes are obscured by charge-transfer bands.[20] Since we could not observe the d–d transitions, we correlated our data with Jorgensen's *f* values[21] (X = Br, Cl, SCN, NCS, NO_2, CN) and obtained coefficients of 0.91 and 0.69 for the oxime methyl and α H resonances, respectively. Thus, our data are more consistent with Busch's explanation than with Hill's. Busch's explanation assumes that the excited states are purely d orbital in character. We will consider this point in more detail later.

A good correlation with Hammett σ functions or the like is reasonable when the effect of X is transmitted to the metal through an organic ligand since the metal-to-ligand bonding is not greatly altered in such series. However, when X is directly bound to the metal, considerable deviations from correlations with organic chemistry must be expected. For this reason and because of the demonstrated similarity of B_{12} models and platinum complexes, we have sought explanations from studies on platinum compounds.

There are some striking similarities between the trends reported in Table I and a variety of spectroscopic and kinetic series found in platinum(II) chemistry.[4] For example, Powell and Shaw[22] observed the following order for hydride chemical shifts in *trans*-$XPt(PEt_3)_2H$ complexes: $NO_3 >$ NCS > Cl > Br > SCN > I > CN. The kinetic trans effect

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(17) G. W. Parshall, *J. Amer. Chem. Soc.*, **86**, 5367 (1964); **88**, 704 (1966); H. A. O. Hill, K. G. Morallee, G. Pellizer, G. Mestroni, and G. Costa, *J. Organmetal. Chem.*, 11, 167 (1968).

(18) E. S. Gore, J. C. Dabrowiak, and D. H. Busch, *J. Chem. Soc., Chem. Commun.*, 923 (1972).

(19) J. S. Griffith and L. E. Orgel, *Trans. Faraday Soc.*, 53, 601 (1951).

(20) G. N. Schrauzer, L. P. Lee, and J. W. Sibert, *J. Amer. Chem. Soc.*, 92, 2997 (1970).

(21) C. K. Jorgensen, "Modern Aspects of Ligand Field Theory," North-Holland Publishing Co., Amsterdam, 1971, p 347.

(22) J. Powell and B. L. Shaw, *J. Chem. Soc.*, 3874 (1965).

has been given as $H_2O \simeq NO_3 < OH < Cl < Br < I \simeq SCN \simeq NO_2 < CN \simeq CH_3 \simeq H$.[4] In platinum chemistry, many variations of this type have been partly attributed to the varying ability of the ligands, X, to compete for metal 6s character in bonding to the metal.[4] Trends of this type are normally not perfect and discrepancies are common. However, usually oxygen donors such as NO_3 and carbon donors such as CH_3 or CN are at the opposite extremes of such series. The ability of ligands to utilize metal s character is dominated by the nature of the ligating atom and increases in the order O < halides < N < S < P < C.[4] There is a clear relationship between the ability of the donor atoms in X to utilize metal s character and the following four trends: the increasing chemical shifts of the oxime methyl resonances in (*t*-Bu(py))Co$(DH)_2$X, the corresponding trend for $(Bu_3P)Co(DH)_2X$,[23] the decreasing chemical shifts of the α H resonances in (*t*-Bu(py))Co$(DH)_2$X, and the increase in J_{P-H} of the $(Bu_3P)Co(DH)_2X$ compounds.

The relationship between the α H chemical shift and the methyl oxime chemical shift is depicted in Figure 2. For the nine compounds[24-26] included in Figure 2, the correlation coefficient is 0.99! Almost beyond question the effect of X on the chemical shift of the α H and the oxime methyl resonances must have a common physical origin. This finding is in conflict with Hill's interpretation. Two points seem certain with regard to the effect of X on the chemical shifts: (1) that the ability of the X ligand to utilize metal s-orbital character is important and (2) that the same physical phenomenon is affecting both the α H and the oxime methyl resonances.

The relative variation of the pmr resonances is consistent with the effect of the anisotropic magnetic susceptibility of the paramagnetic currents on the neighboring cobalt ion. If one assumes the screening formula of an axially anisotropic group[27] for the cobalt center (axis coincident with the molecular pseudo C_4 axis) then one predicts the variation in shieldings of different ligand resonances to be linearly related with slopes dependent on the ratio of the term $(1 - 3\cos^2\theta)/R^3$ for the two resonances averaged over internal molecular motions, where R is the distance from the cobalt ion and θ is the angle made with the symmetry axis. We have calculated the slope predicted by this geometric relationship to be -2.0. This calculation used distances available from crystallographic data;[28] however, we took the precaution[29] of using a C–H bond length of 1.08 Å. The slope in Figure 2 has a value of −1.6 ± 0.2. The agreement with theory is therefore quite good, especially since the geometric expression employed was based on a point dipole model and the difficulty of accurately positioning hydrogen atoms from crystallographic data. This geometric expression was also used by Gore, Dabrowiak, and Busch[18] but reportedly gave poor agreement with experiment.[29a]

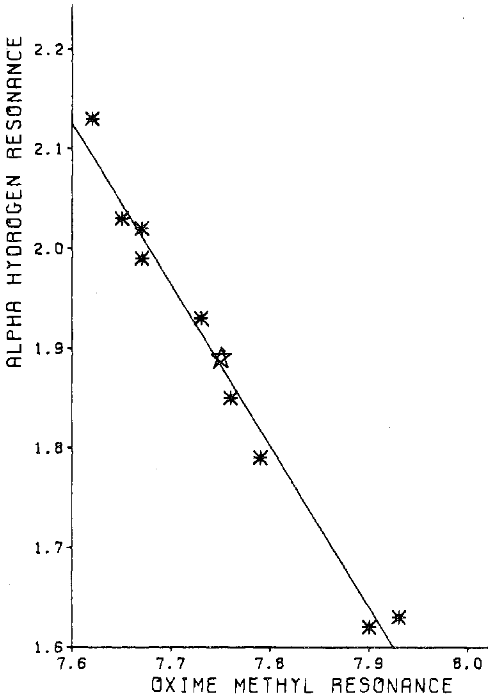

Figure 2. Plot of the α H pmr signals *vs.* the oxime methyl pmr signals (in τ units) for (*t*-Bu(py))Co$(DH)_2$X compounds.[24] The least-squares line is drawn and the mean value of the data is indicated by the star. The points (from top to bottom) are for X = NO_3, NCS, Br, Cl, NO_2, *i*-PrXan, CN, CH_3, and $(CH_3O)_2P(O)$, respectively. The equation of the line is $Y = 14.41 - 1.62X$.

We will now discuss how the *magnitude* of the anisotropy is affected by X. When one goes from O_h to C_{4v} symmetry, the low-lying unoccupied e_g* molecular orbitals of predominantly metal d_{z^2} and $d_{x^2-y^2}$ character (*z* direction along C_4) are split into an a_1* (mainly d_{z^2}) and b_1* (mainly $d_{x^2-y^2}$) pair. Paramagnetic anisotropy is proportional to the mixing of the two low-lying excited states (which approximately correspond to promotion of an electron to a_1* or b_1*) with the ground state, coupled by the orbital angular momentum operators.[30] But the metal s orbital is also of a_1 symmetry and so the a_1* orbital will have metal s orbital character mixed in. This lowers the angular momentum matrix element with the corresponding excited state and, hence, its contribution to paramagnetic shielding. Increased covalency in the metal–ligand bond should have a similar effect[31] since the a_1* MO is not of pure metal character but involves a small variable contribution from ligand σ orbitals. This contribution increases with the covalency of the bond. These

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(23) The ligand X will compete for metal s character strongly with the trans ligands *t*-Bu(py) and Bu_3P. The ligand Bu_3P is a better competitor for metal 4s character than is *t*-Bu(py). Therefore, the type of leveling effect discussed in ref 4 occurs for the $(Bu_3P)Co(DH)_2X$ series.

(24) Some explanation of the reasons for using these nine compounds is in order. Figure 1 includes data for (*t*-Bu(py))Co$(DH)_2$-$P(O)(OCH_3)_2$, which will be described elsewhere. Such P-bonded dialkylphosphonates are known to have a strong trans influence,[25] presumably as the result of strong σ-bond formation to metals. Our rate studies[26] reveal that the ligand has a trans-labilizing effect comparable to CH_3. This similarity is reflected in the chemical shifts of the α H and oxime methyl resonances, τ 1.62 and 7.90, respectively. The compounds with X = N_3 and X = SCN are well off the line. We realized the significance of this result when we studied (*t*-Bu(py))Co$(DH)_2$SeCN (generously supplied by Dr. John L. Burmeister). This compound gave a pmr spectrum in which the α H and methyl oxime resonances were located at τ 1.87 and 7.64, respectively. Thus, all three compounds containing linear triatomics which form a bent bond to cobalt (N_3, SCN, SeCN) are similarly off the line. The α H resonances are in keeping with the nature of the donor atom. Therefore, we feel that the anisotropy of the bent-bonded triatomic ligands, which spatially are in close proximity to the oxime methyl groups, is affecting the shifts of the oxime methyl resonances. Unfortunately, this anomaly precludes any conclusion about differences in bonding between the thiocyanate linkage isomers.

(25) G. G. Mather and A. Pidcock, *J. Chem. Soc., Dalton Trans.*, 560 (1973).

(26) W. C. Trogler, R. C. Stewart, and L. G. Marzilli, *J. Amer. Chem. Soc.*, 96, 3697 (1974).

(27) H. M. McConnell, *J. Chem. Phys.*, 27, 226 (1957).

(28) P. G. Lenhert, *Chem. Commun.*, 980 (1967); W. W. Adams and P. G. Lenhert, *Acta Crystallogr., Sect. B*, 29, 2412 (1973).

(29) M. R. Churchill, *Inorg. Chem.*, 12, 1213 (1973).

(29a) Note Added in Proof. An increase in θ for the α hydrogens of only 1.6° (44.5° → 46.1°) results in perfect agreement between theory and experiment.

(30) N. F. Ramsey, *Phys. Rev.*, 77, 567 (1950); 86, 243 (1952).

(31) S. Fujiwara, F. Yajima, and A. Yamasaki, *J. Magn. Resonance*, 1, 203 (1969).

effects appear in the numerator of Ramsey's formula for paramagnetic current effects and cannot be ignored. Reduction of this numerator[32] is the same as if the denominator (ligand field splitting) were larger than the measured value.

Our work differs from that of Gore, Dabrowiak, and Busch[18] in the following respects. First, the Co(macrocycle)X_2^+ complexes are apparently sufficiently ionic to allow the usual procedure of correlating data solely with the spectrochemical series. Second, the large *opposite* shifts observed for the in-plane and out-of-plane ligand protons provide strong support for both treatments. Suitable out-of-plane protons were not present in Busch's compounds.

On the basis of our results, particularly those with $X^- = CN^-$, we conclude that attributing a low oxidation state to cobalt in alkylcobaloximes is probably not correct. Rather, it is preferable to consider the cobalt center in alkylcobaloximes to be hybridized differently from other cobaloximes. The alkylcobaloximes are not at the extreme of rehybridization since Schrauzer[33] has found that $Bu_3PCo(DH)_2H$ (in hexane) exhibits an oxime methyl resonance at $\tau \sim 9$. This result improves the correlation of oxime methyl chemical shift with the trans effect series for platinum(II).[34]

Experimental Section

All chemicals used were of reagent grade or higher purity. Methylene chloride was Fisher Certified reagent grade. The instruments used were Varian A-60 and JEOL MH100 nmr spectrometers. Results for the oxime methyl resonance of the (*t*-Bu(py))Co(DH)$_2$X complexes were comparable for both instruments. The MH100 was operated in internal mode with the solvent signal used as a lock. Ir spectra were recorded using KBr disks and either a Perkin-Elmer 337 or 457 grating instrument.

Preparations. I. Co(DH)(DH$_2$)Cl$_2$. This complex is a known species,[11] and the following procedure was found most convenient. Cobaltous chloride hexahydrate (50 g, 0.210 mol) was dissolved in acetone (1.5 l.) and dimethylglyoxime (49 g, 0.422 mol) was added. The mixture was agitated for 10 min and filtered to remove any undissolved material. The green crystals formed when the solution was allowed to stand overnight were collected and washed with acetone; yield 59.5 g (79%). No aeration was necessary.

(py)Co(DH)$_2$Cl. A suspension of Co(DH)(DH$_2$)Cl$_2$ (3.3 g, 0.009 mol) in chloroform (85 ml) was shaken with pyridine (1.8 g). After a few minutes, water (30 ml) was added to the flask and the chloroform layer was vigorously stirred (magnetic mixer) for 2 hr. The aqueous layer was discarded and the chloroform layer filtered and extracted with water until the washings were nearly colorless. The solution was reduced in volume and the product precipitated by addition of ethanol (95%). The brown complex was recrystallized from methylene chloride by adding ethanol; yield 67%. *Anal.* Calcd for $C_{13}ClCoH_{19}N_5O_4$: C, 38.9; H, 4.7; Co, 14.6. Found: C, 38.8; H, 5.0; Co, 14.7.

This procedure has been found to work well for a large number of ligands. A modification used was to substitute a strong noncoordinating base (tri-*n*-butylamine) for an excess of ligand. A more convenient procedure which has *not* been checked using other ligands is given below for (*t*-Bu(py))Co(DH)$_2$(halide).

(*t*-Bu(py))Co(DH)$_2$Cl. The complex [Co(DH)(DH$_2$)Cl$_2$] (18.05 g, 0.05 mol) was suspended in absolute methanol (200 ml) and the mixture heated to 60° with stirring. After a few minutes, tri-*n*-butylamine (9.5 g) was added and all the complex dissolved. A solution of 4-*tert*-butylpyridine (7.0 g) in methanol (20 ml) was added, and after 5 min the solution was diluted with water (40 ml). This mixture was kept warm for 15 min and then set aside for crystallization to occur. The brown crystals were collected, washed with acetone, and air-dried; yield 19.1 g (83%). *Anal.* Calcd for $C_{17}CoClH_{27}N_5O_4$: C, 44.4; H, 5.9; Co, 12.8. Found: C, 44.4; H, 6.1; Co, 12.9.

The Br complex was prepared in an analogous manner. *Anal.* Calcd for $BrC_{17}CoH_{27}N_5O_4$: C, 40.5; H, 5.4; Co, 11.7. Found: C, 40.7; H, 5.3; Co, 11.7.

(*t*-Bu(py))Co(DH)$_2$CNS. The complex (*t*-Bu(py))Co(DH)$_2$Cl (9.2 g), prepared by either method, was suspended in 80% methanol–water (200 ml), and the mixture was warmed gently for 5 min. A solution of KSCN (1.94 g) in water (20 ml) was added, whereupon all the chloro complex dissolved, and heating was continued for 5 min. After the solution was diluted with water (100 ml) and cooled in ice for 15 min, the brown crystals formed were collected. These were dissolved in 80% methanol–water (200 ml) and the solution heated for 5 min before the addition of a solution of KSCN (0.97 g) in water (20 ml). The solution was kept at near boiling for 15 min and then cooled in an ice bath. The crystals formed were collected (7.64 g). Water (100 ml) was added to the filtrate and a second fraction (1.09 g) was obtained; combined yield 91%.

Fractional Crystallization of Isomers. The complex (*t*-Bu(py))Co(DH)$_2$CNS (4.0 g) was dissolved in methylene chloride (50 ml) and the solution was treated with hexane (50 ml). After 30 min, more hexane (50 ml) was added and isomerically pure (*t*-Bu(py))Co(DH)$_2$NCS separated (2.66 g). The filtrate was allowed to stand overnight and much of the methylene chloride and some of the hexane evaporated. The precipitate (0.4 g) was 80% N-bonded and 20% S-bonded material. Dark crystals which appeared in the precipitate proved to be pure S-bonded isomer. Methylene chloride (50 ml) and hexane (10 ml) were added to bring the filtrate back to the original volume and then more hexane (100 ml) was added. The precipitate formed (0.6 g) again contained dark crystals of the S-bonded isomer. The filtrate was then set aside to allow the methylene chloride to evaporate. The product obtained (0.2 g) was (>90%) isomerically pure (*t*-Bu(py))Co(DH)$_2$SCN. *Anal.* Calcd for $C_{18}CoH_{27}N_6O_4S$: C, 44.8; H, 5.6; Co, 12.2. Found (*N*CS): C, 44.5; H, 6.0; Co, 12.1. Found (*S*CN): C, 45.0; H, 6.0; Co, 12.2.

(*t*-Bu(py))Co(DH)$_2$CN. Initial preparations yielded mainly K[Co(DH)$_2$(CN)$_2$]. It was determined that the cobalt(II) present was largely responsible and therefore $BrCCl_3$ was used to oxidize any cobalt(II) that might be present. The complex (*t*-Bu(py))Co(DH)$_2$Cl (3.5 g, 0.0076 mol) was heated in methanol (150 ml, containing 5 ml of $BrCCl_3$) for 15 min. Potassium cyanide (0.52 g) was added and, after 25 min, water (25 ml). After the solution had been standing overnight, the orange crystals formed were collected and recrystallized from methylene chloride by addition of ethanol (95%); yield 1.5 g (44%). The infrared spectrum of this compound exhibits a very sharp weak band at 2140 cm^{-1}. *Anal.* Calcd for $C_{18}CoH_{27}N_6O_4$: C, 48.0; H, 6.0; Co, 13.1. Found: C, 47.5; H, 5.9; Co, 13.1.

(*t*-Bu(py))Co(DH)$_2$N$_3$. The complex (*t*-Bu(py))Co(DH)$_2$Cl (1 g) was dissolved in methanol (80 ml) and the solution treated with a solution of sodium azide (0.2 g) in water (5 ml). After 15 min, the solution was filtered and water was added with stirring. The product was collected, washed with water, and air-dried. It was recrystallized by adding aqueous methanol to a methylene chloride solution. *Anal.* Calcd for $C_{17}CoH_{27}N_8O_4$: C, 43.8; H, 5.8; Co, 12.6. Found: C, 43.4; H, 5.7; Co, 12.7.

Preparations. II. Complexes described in this section were prepared as nearly as possible according to the directions given in ref 9 and 35.

[(py)$_2$Co(DH)$_2$][Co(DH)$_2$Cl$_2$]. The procedure described in ref 9 for the preparation of (py)Co(DH)$_2$Cl was followed. The product obtained (70% yield) was too insoluble to permit observation of the pmr spectrum in methylene chloride, whereas (py)Co(DH)$_2$Cl gave a single resonance at τ 7.65. The ir spectra of both materials are identical except for a small to medium sharp peak at 1155 cm^{-1} in the salt. Heating a suspension of [(py)$_2$Co(DH)$_2$][Co(DH)$_2$Cl$_2$] in chloroform (containing several drops of $BrCCl_3$) in contact with an aqueous solution of As(C$_6$H$_5$)$_4$Cl resulted in the formation of a brown aqueous phase. (A similar experiment with (py)Co(DH)$_2$Cl led to a clear aqueous phase.) Filtration of the chloroform suspension revealed a colored solution. Treatment of this solution with

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[32] Axial anisotropy arises since the screening tensor (σ_p) due to the paramagnetic currents on cobalt is axially symmetric. By expressing d_{z^2} and $d_{x^2-y^2}$ as linear combinations of the appropriate imaginary orbitals, which are eigenfunctions of L_z ($d_{z^2} = d_0$ and $d_{x^2-y^2} = {}^1/_2(d_{+2} + d_{-2})$) and by representing L_x and L_y as combinations of the raising and lowering operators (*e.g.*, $L_x = {}^1/_2(L^+ + L^-)$) one can demonstrate that the d_{z^2} orbital makes equal contributions to $\sigma_{p,xx}$ and $\sigma_{p,yy}$ and no donation to $\sigma_{p,zz}$. The s-orbital character of the a_1^* orbital makes zero contribution. Similarly, $d_{x^2-y^2}$ contributes chiefly to $\sigma_{p,zz}$ and to a smaller equal degree to $\sigma_{p,xx}$ and $\sigma_{p,yy}$. The b_1^* orbital will vary slightly compared to a_1^* as the axial ligands are changed. Thus, varying the axial ligands affects metal s-orbital contribution to a_1^* which inherently influences the per cent d_{z^2} orbital character of a_1^* and affects $\sigma_{p,xx}$ and $\sigma_{p,yy}$ accordingly.

[33] G. N. Schrauzer and R. J. Holland, *J. Amer. Chem. Soc.*, 93, 1505 (1971).

[34] The correlation with the kinetic trans effect is improved if one considers [(*t*-Bu(py))Co(DH)$_2$H$_2$O]NO$_3$, which has an oxime methyl resonance at τ 7.54. This species is not included in Table I because it is charged and, unless partially dihydrated to (*t*-Bu(py))Co(DH)$_2$NO$_3$, is not soluble in CH_2Cl_2.

ethanol permitted isolation of the salt $As(C_6H_5)_4[Co(DH)_2Cl_2]$, which was identified by its ir and pmr spectra, the latter confirmed by addition of the salt $As(C_6H_5)_4[Co(DH)_2Cl_2]$ to the pmr tube (methyl resonance occurs at τ 7.63). If $BrCCl_3$ is not added to the chloroform solution of $(py)Co(DH)_2$, $As(C_6H_5)_4[Co(DH)_2Cl_2]$ can be isolated. (The resonances of anionic and cationic complexes depend to some extent on the counterion in nonpolar solvents.) *Anal.* Calcd for $C_{26}Cl_2Co_2H_{38}N_{10}O_8$: C, 38.9; H, 4.7; Co, 14.7. Found: C, 38.5; H, 4.7; Co, 14.4.

$[(t\text{-}Bu(py))_2Co(DH)_2][Co(DH)_2Cl_2]$. The ir spectrum of this complex and that of the isomer reported above are virtually identical. This salt has a pmr spectrum consistent with the proposed structure. It could be converted into $As(C_6H_5)_4[Co(DH)_2Cl_2]$ as described for the pyridine salt. *Anal.* Calcd for $C_{34}Cl_2Co_2H_{56}N_{10}O_8$: C, 44.4; H, 6.1; Co, 12.9. Found: C, 44.2; H, 5.8; Co, 12.9.

$[(t\text{-}Bu(py))_2Co(DH)_2][Co(DH)_2(CNS)_2]$. This material, prepared according to procedures described in ref 9 and 35, was the product which remained after the aerial oxidation product was washed with methylene chloride. The product was sufficiently soluble in dimethylformamide to permit observation of the pmr spectrum. The resonances (relative to TMS, relative intensities in parentheses) were found at τ 8.77 (1.5), 7.64 (1.0), 7.62 (0.2), 7.59 (0.4), and 7.56 (0.4). These resonances are consistent with the presence of the $(t\text{-}Bu(py))_2Co(DH)_2^+$ cation and the three isomers of $Co(DH)_2(CNS)_2^-$. As before, the $As(C_6H_5)_4^+$ salt of the anion could be isolated and identified. *Anal.* Calcd for $C_{36}Co_2H_{54}N_{12}O_8S_2$: C, 44.8; H, 5.6; Co, 12.2. Found: C, 44.5; H, 6.0; Co, 12.0. The infrared spectrum of this salt is virtually identical with that of $(t\text{-}Bu(py))Co(DH)_2NCS$ with which it may be easily confused. Preliminary studies suggest that the analogous pyridine salt also exists, and the presence of this salt may have contributed to the different results reported in published reports of the $(py)Co(DH)_2CNS$ isomers.[36]

Preparations. III. Miscellaneous Section. $(t\text{-}Bu(py))Co(DH)_2NO_2$. A mixture of dimethylglyoxime (4.64 g) and cobaltous acetate tetrahydrate (5.60 g) in ethanol (200 ml) was heated to near boiling. A solution of 4-*tert*-butylpyridine (3 ml, 2.7 g) dissolved in ethanol (50 ml) was added, followed by a solution of sodium nitrite (1.38 g in water, 10 ml). This mixture was warmed and stirred for 1 hr and aerated for 2 hr. The solution was filtered and the filtrate set aside for 2 days. As the solution evaporated, reddish brown crystals formed; yield 0.66 g. *Anal.* Calcd for $C_{17}CoH_{27}N_6O_6$: C, 43.4; H, 5.8; Co, 12.5. Found: C, 43.4; H, 5.8; Co, 12.4.

$(t\text{-}Bu(py))Co(DH)_2CH_3$. The procedure described by Hill[1] was employed, using $(t\text{-}Bu(py))Co(DH)_2Cl$. *Anal.* Calcd for $C_{18}CoH_{30}N_5O_4$: C, 49.2; H, 6.9; Co, 13.4. Found: C, 49.4; H, 7.0; Co, 13.4.

$(t\text{-}Bu(py))Co(DH)_2(i\text{-}PrXan)$. The preparative procedure described in ref 9 gave the desired compound. *Anal.* Calcd for $C_{21}CoH_{34}N_5O_5S_2$: C, 45.1; H, 6.1; Co, 10.5. Found: C, 45.0; H, 6.1; Co, 10.5.

$As(C_6H_5)_4[Co(DH)_2Cl_2]$: A solution of $As(C_6H_5)_4Cl$ (2.5 g) in water (100 ml) was added with rapid stirring to a solution of $H[Co(DH)_2Cl_2]$ (1.9 g) in water (100 ml). The golden yellow crystals formed were collected, washed with methanol, and recrystallized by dissolving them in methylene chloride and adding ethanol. The recrystallized product was dried in air; yield 1.2 g. *Anal.* Calcd for $AsC_{32}Cl_2CoH_{34}N_4O_4$: C, 51.7; H, 4.6; Co, 7.9. Found: C, 51.6; H, 4.1; Co, 7.9.

$As(C_6H_5)_4[Co(DH)_2(NO_2)_2]$. Dimethylglyoxime (4.65 g, 0.04 mol) was added to a solution of cobaltous acetate tetrahydrate (5.0 g, 0.02 mol) in warm ethanol ((95%), 250 ml). This mixture was boiled for 2 min with stirring before sodium nitrite (3.1 g, 0.045 mol) was added. The solution was stirred for 1 hr and then cooled and filtered. The filtrate was treated with $As(C_6H_5)_4Cl \cdot xH_2O$ (2.8 g); ether (500 ml) was added slowly, and the thick precipitate formed was collected. This product was dissolved in methylene chloride and the solution filtered. Careful addition of ether produced brown crystals, which were collected, washed with ether, and dried in a desiccator; yield 2.3 g (68%). *Anal.* Calcd for $AsC_{32}CoH_{34}N_6O_8$: C, 50.3; H, 4.5; Co, 7.7. Found: C, 50.5; H, 4.6; Co, 8.1.

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Registry No. $(t\text{-}Bu(py))Co(DH)_2NO_3$, 51194-55-9; $(t\text{-}Bu(py))Co(DH)_2NCS$, 51261-65-5; $(t\text{-}Bu(py))Co(DH)_2N_3$, 51194-56-0; $(t\text{-}Bu(py))Co(DH)_2Br$, 51194-57-1; $(t\text{-}Bu(py))Co(DH)_2Cl$, 38985-28-3; $(t\text{-}Bu(py))Co(DH)_2SCN$, 51261-66-6; $(t\text{-}Bu(py))Co(DH)_2NO_2$, 51194-34-4; $(t\text{-}Bu(py))Co(DH)_2(i\text{-}PrXan)$, 51194-35-5; $(t\text{-}Bu(py))Co(DH)_2CN$, 51212-02-3; $(t\text{-}Bu(py))Co(DH)_2CH_3$, 51194-36-6; $(Bu_3P)Co(DH)_2NO_3$, 51194-37-7; $(Bu_3P)Co(DH)_2NCS$, 51194-38-8; $(Bu_3P)Co(DH)_2N_3$, 51194-39-9; $(Bu_3P)Co(DH)_2Br$, 51194-40-2; $(Bu_3P)Co(DH)_2Cl$, 24501-27-7; $(Bu_3P)Co(DH)_2SCN$, 51194-41-3; $(Bu_3P)Co(DH)_2NO_2$, 51194-42-4; $(Bu_3P)Co(DH)_2(i\text{-}PrXan)$, 51194-43-5; $(Bu_3P)Co(DH)_2CN$, 51194-44-6; $(Bu_3P)Co(DH)_2CH_3$, 51020-41-8; $(py)Co(DH)_2Cl$, 23295-32-1; $As(C_6H_5)_4[Co(DH)_2Cl_2]$, 51194-45-7; $As(C_6H_5)_4[Co(DH)_2(NO_2)_2]$, 51194-46-8; $(1\text{-}MeImd)Co(DH)_2(ONO)$, 51194-47-9; $(1\text{-}MeImd)Co(DH)_2(NO_2)$, 51194-48-0; $Co(DH)(DH_2)Cl_2$, 23638-66-6; py, 110-86-1.

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(35) One of the referees had prepared $(py)Co(DH)_2Cl$ and had obtained the desired product using the ref 9 preparation. If one is to prepare one or two cobaloxime complexes, the Schrauzer preparations should be tried first. However, when $Co(DH)(DH_2)Cl_2$ is on hand, the preparations reported here can be completed more rapidly.

(36) A. H. Norbury and A. I. P. Sinha, *Inorg. Nucl. Chem. Lett.*, 4, 617 (1968); A. H. Norbury, P. E. Shaw, and A. I. P. Sinha, *Chem. Commun.*, 1080 (1970); R. L. Hassel and J. L. Burmeister, *ibid.*, 568 (1971).