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Contribution from the Department of Chemistry,
University of Delaware, Newark, Delaware 19711

New Insights Concerning the Trans Influence Based upon the Linkage Isomeric Ratios of Thiocyanate in Cobaloxime Complexes[1]

JOSEPH A. KARGOL, KAREN D. LAVIN, ROGER W. CRECELY, and JOHN L. BURMEISTER*

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The linkage isomeric ratios for thiocyanate trans to various donors have been determined for a series of cobaloxime complexes[*trans*-bis(dimethylglyoximato)(ligand)(thiocyanato)cobalt(III)] by utilizing proton NMR measurements. The chemical shift of the methyl protons of the dimethylglyoximate group is sensitive to the nature of the axial ligands, the τ values of the S-bound isomers being ca. 0.1 ppm less than those of the N-bound isomers in an aromatic solvent such as nitrobenzene. It was found that the presence of a small amount of Co(II) is necessary in order to facilitate isomerization and the attainment of equilibrium. The ratio of sulfur- to nitrogen-bound species, K(S/N), is related to the trans influence and the basicity of the trans ligands. The observed order of decreasing trans influence is roughly the following: alkyls $\gg$ phosphites $\approx$ pyridines > anilines > phosphines > thioureas, K(S/N) decreasing in the reverse order. Within the pyridine, aniline, and phosphine series, K(S/N) decreases as the pK_a of the trans ligand increases. Greater through-space P–H coupling is present for phosphorus donors trans to S-bound thiocyanates than to N-bound thiocyanates. The bridging ability in inner-sphere electron-transfer reactions for the three ions studied decreases in the order NCS$^-$ > CN$^-$ > NO$_2^-$. The influence of solvent upon K(S/N) and the clarification of some discrepancies concerning previously reported cobaloximes are also discussed.

Introduction

Much recent interest[2-12] has been shown in the application of NMR spectroscopy to elucidate the bonding mode of thiocyanate (SCN$^-$) and the consanguineous ions selenocyanate (SeCN$^-$) and cyanate (OCN$^-$) in transition-metal complexes. These experiments have utilized direct measurements of ^{13}C,[2] ^{14}N,[3] ^{15}N,[4] and ^{77}Se[5] NMR spectra and indirect measurements for ^{1}H,[6-9] ^{31}P,[10-12] and other nuclei. In general, these efforts have been directed toward understanding the various factors which influence the bonding modes of the pseudohalides. Because of the intimacy with which the bonding mode of thiocyanate and its chemical environment are related, the ion has experienced considerable use as a chemical probe.[13,14]

A large number of studies have been reported concerning the trans effect[15] or trans influence[15] in *trans*-bis(dimethylglyoximato)cobalt(III) complexes, otherwise known as cobaloximes and symbolized by the general formula Co(DH)$_2$BX (DH = monoionized dimethylglyoxime; B and X are various other ligands).[16-22] In one of these cases,[21] the trans effect and trans influence have been shown to be comparable for octahedral complexes.

Similarly, much has been published regarding the bonding of SCN$^-$, SeCN$^-$, and OCN$^-$ in cobaloximes.[6,7,23-27] Marzilli et al.[6] have presented evidence which suggests that the bonding mode of thiocyanate in cobaloximes is related to the trans influence of the other axial ligands. Later, Norbury et al.[7] presented data which appeared to be in conflict with these observations. The major difference between these two studies is the presence[6] (or absence[7]) of Co(II) in the solutions of the complexes which were studied. Marzilli[28] has also shown that the Co–SCN/Co–NCS linkage isomeric ratio is sensitive to the dielectric constant of the solvent in which the cobaloxime–thiocyanate complex is dissolved. The present study was undertaken in an attempt to clarify the discrepancies noted above and also to provide data for a wider variety of ligands, both with regard to the trans influence and to solvent control of the thiocyanate bonding mode.

Experimental Section

Preparation of Complexes. All chemicals and solvents used were of reagent grade or better. The nitrobenzene used was examined via ^{1}H NMR at high sensitivity. Its spectrum was found to be free of any spurious resonances in the region of interest.

The method of Norbury et al.[7] was used to prepare complexes with pyridine (py), 4-cyanopyridine (4-CN-py), 4-acetylpyridine (4-ac-py), 4-aminopyridine (4-NH$_2$-py), 3-methylpyridine (3-pic), 4-methylpyridine (4-pic), piperidine (pip), imidazole (im), isoquinoline (iqn), aniline (an), 2-ethylaniline (2-Et-an), 4-bromoaniline (4-Br-an), 3-fluoroaniline (3-F-an), 4-fluoroaniline (4-F-an), 2-chloroaniline

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(15) The terms trans effect and trans influence have often wrongly been used interchangeably. The trans influence of a ligand pertains to its ability to weaken the bond of the opposite ligand, while the trans effect of a ligand relates to its effect on the rate of replacement reactions of the opposite ligand. While the available evidence now suggests that these two properties are the same for octahedral complexes, this is not always the case with other geometries.

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(2-Cl-an), 4-methylaniline (4-Me-an), 3-nitroaniline (3-NO_2-an), and 2,5-dimethoxyaniline ($(MeO)_2$-an). It was found necessary to recrystallize many of these complexes in acetone or methanol in order to obtain analytically pure samples. For some complexes, such as that with piperidine, washing steps were omitted due to the high solubility of the compound. For these cases, recrystallization in acetone or dichloromethane was substituted. Sodium hexanitrocobaltate(III) was either obtained commercially or prepared via an established route.[29] The procedures outlined by Tschugaeff[30] were followed to prepare $Na[Co(DH)_2(NO_2)_2]$, $Co(DH)(DH_2)(NO_2)_2$, and $Co(DH)_2(H_2O)(NO_2)$. By addition of concentrated HCl to $Na[Co(DH)_2(NO_2)_2]$ after filtration of unreacted dimethylglyoxime, $Co(DH)(DH_2)(NO_2)_2$ could be prepared without the isolation of the sodium salt.

The complexes with *N,N'*-ethylenethiourea (etu), *N,N'*-dimethylthiourea (dmtu), *N,N'*-diethylthiourea (detu), methylthiourea (mmtu), and thioacetamide (taa) were prepared by using the method of Schrauzer.[31] The etu, dmtu, and detu complexes gave satisfactory analyses without recrystallization. For mmtu and taa, it was necessary to recrystallize the complexes from methanol. Attempts to produce complexes with *N,N'*-dibutylthiourea and *N,N'*-diisopropylthiourea failed to give any product, apparently due to steric effects. The reaction with thiourea gave a solid which did not give an acceptable analysis, even after recrystallization. Attempts to produce thiourea-type complexes by the method of Norbury et al.[7] were also unsuccessful. The complex with 5-nitroisoquinoline (5-NO_2-iqn) was also prepared by the Schrauzer method.[31]

The *tert*-butylpyridine (4-*t*-Bu-py) complex was prepared via a published route.[32] When the addition of hexane failed to precipitate the desired product, the solution was placed in an evaporating dish. After 7.5 h, the solution was transferred to a smaller evaporating dish. Any solid precipitate was redissolved in methylene chloride and added to the original filtrate. The solution was set aside as before and evaporated to dryness. Needlelike dark brown crystals of the desired product formed at the top of the dish, with the material at the bottom being more amorphous in appearance. The crystals from the top of the evaporating dish were removed manually with a spatula. This complex was obtained as the S isomer.

$Co(DH)_2(NH_3)(SCN)\cdot H_2O$ was synthesized by a method similar to those discussed elsewhere.[7,33] Concentrated ammonium hydroxide was added to a solution prepared as described in the references until a yellow-brown precipitate formed. The solid was then isolated by suction filtration.

The method of Ablov et al.[34] was used to attempt the preparation of $Co(DH)_2(H_2O)(SCN)\cdot H_2O$. Analysis of this complex revealed that the product was, in fact, the ammine monohydrate. Because this synthesis was also used by Norbury et al.,[7] our results cast some doubt as to whether the complex they isolated was the aquo monohydrate or the ammine monohydrate (vide infra).

A literature method[31] was used to prepare $Co(DH)_2(CH_3)(SMe_2)$ (as well as the analogous ethyl and propyl compounds). This was treated in the same manner as that in which Dodd and Johnson used $Co(DH)_2(CH_3)(H_2O)$[23] to give $TPA[Co(DH)_2(CNS)(CH_3)]$ (TPA = tetraphenylarsonium). The product was recrystallized from methanol.

Benzyltriphenylphosphonium chloride (BBP-Cl) was made by a route similar to that reported by Grimshaw and Ramsey.[35] Equivalent amounts of triphenylphosphine and benzyl chloride were refluxed for 15 h in chloroform. The chloroform was evaporated to approximately one-fourth its initial volume, at which time crystals began forming. Addition of diethyl ether caused further precipitation. The product was removed by filtration and washed with diethyl ether. Recrystallization was carried out in ethanol.

$BBP[Co(DH)_2(CNS)_2]$ was prepared in a manner similar to the method previously reported.[36] This complex was recrystallized from methanol. No attempt was made to prepare a sample which contained only one of the three possible linkage isomers.

$BPP[Co(DH)_2(NO_2)_2]$ was prepared by treating a 50% ethanol–water solution of the sodium salt with benzyltriphenylphosphonium chloride. The orange microcrystalline product was recrystallized three times from methanol to give red crystals. The method of Norbury et al.[7] was used to attempt the preparation of $Et_4N[Co(DH)_2(NO_2)(NCS)]$. A dark brown material was obtained which exhibited a broad band in the infrared spectrum at 2132 cm^{-1}. This apparently corresponds to the 2130-cm^{-1} band observed by Norbury et al.,[7] which was attributed to a ν_{CN} peak for an N-bonded complex. $BPP[Co(DH)_2(NO_2)(NCS)]$ was prepared by initiating the reaction according to Norbury et al.[7] After filtration of the aqueous solution of $K[Co(DH)_2(NO_2)(CNS)]$ to remove unreacted material, the volume of solution was reduced under vacuum to give a solid product. The infrared spectrum of this gave a ν_{CN} band at 2099 cm^{-1} (due to the S-bound isomer) with a high frequency shoulder. Recrystallization of this solid gave a product with only one ν_{CN} band, now at 2109 cm^{-1}. This shift in the ν_{CN} band is indicative of an isomerization of the solid from S bonding to N bonding. There was no evidence of a low-frequency shoulder which should be evident if any S-bound material was still present.

$Co(DH)_2PPh_3$ was synthesized via the method of Schrauzer and Lee.[37] The $BPP[Co(DH)_2(CN)(SCN)]$ complex was prepared via the method of Crumbliss and Gaus[38] by using bis(dimethylglyoximato)(thiocyanato)(4-cyanopyridine)cobalt(III). The 4-cyanopyridine ligand provides a better leaving group and also allows one to check the product for the presence of starting material, on the basis of whether or not a ν_{CN} band arising from the 4-cyano group is observed in the IR spectrum.

The attempted preparation of $TPA[Co(DH)_2(CN)_2]$ was carried out by using the method of Crumbliss and Gaus.[39] Although the IR spectral data for this material was in agreement with that reported for the desired product,[38,39] this material failed to give an acceptable analysis for carbon, despite repeated recrystallizations. Special instructions[40] were sent to the analyst with the thought that complete combustion for the sample had not been attained. A higher combustion temperature, 1050 °C, and the use of V_2O_5 improved the carbon analysis somewhat. A proton NMR spectrum gave only one peak for the oxime methyl protons, indicating that the analytical difficulties may be due to cationic impurities or incomplete combustion.

Phosphine and phosphite complexes were generated in situ via previously described ligand-exchange reactions.[6] The phosphorus ligands were added to 0.05 M solutions of $Co(DH)_2(4\text{-CN-py})(SCN)$ with the appropriate amount of $Co(DH)_2PPh_3$ added.

Physical Measurements. All infrared measurements were made by using a Perkin-Elmer 180 spectrometer. Routine measurements made for characterization purposes were obtained by using Nujol mulls and KBr disks. Solution IR measurements were made with matched CaF_2 solution cells. Solid-state ν_{CN} integrated absorption values were obtained by using the method of Bailey,[41] as adapted by Hassel and Burmeister.[42] The molar conductances of neutral cobaloximes were determined at 25 °C with an Industrial Instruments, Inc., Model RC-16B2 conductivity bridge, using 10^{-3} M nitrobenzene solutions. All conductances were found to be well below the range for 1:1 electrolytes.[43] Decomposition points were determined by using a Thomas-Hoover melting point apparatus and are uncorrected. The decomposition point was taken to be the temperature at which the compound either melted or discolored. Proton NMR data were obtained at 35 °C for 0.05 M solutions of the complexes in nitrobenzene, unless otherwise noted. A small amount of Co(II) was added to each sample in the form of $Co(DH)_2PPh_3$ [ratio of 1:200 Co(II) to complex]. Samples were allowed to equilibrate for a minimum of 1 h. (Some samples required longer time periods.) The samples were kept in the tube warmer of the NMR instrument for 0.5 h prior to measurement to ensure that the samples were at the probe temperature. The instrument used to make most of the measurements

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Table I. Analytical and Physical Data for Isolated *trans*-$[Co(DH)_2(L)(CNS)]$ Complexes

L[a]	% calcd		% found		dec pt, °C	ν_{CN},[j] cm^{-1} (Nujol mull)
	C	H	C	H		
py	49.44	4.49	49.12	4.46	240	2117
4-ac-py	41.03	4.52	41.34	4.73	231	2120 (2040)
4-NH_2-py	38.10	4.65	38.40	4.59	246	2106
4-CN-py	39.92	4.02	39.96	4.00	208	2122 (2038)
3-pic	40.92	4.77	41.04	4.85	219	2110
4-pic	40.92	4.77	40.25	4.72	208	2118
4-*t*-Bu-py	44.81	4.64	44.79	5.81	217	2109
pip	38.89	5.83	38.07	5.73	178	2120 (2023)
iqn	45.39	4.44	45.07	4.49	197	2119, 2123
5-NO_2-iqn	41.47	4.06	41.67	4.16	234	2124
im	34.71	4.37	34.40	4.18	219	2127
an	40.91	4.81	40.72	4.93	232	2121
4-Br-an	34.70	3.88	34.58	3.98	118	2113
2-Cl-an	37.95	4.25	38.85	4.47	183	2114
4-Me-an	42.30	5.10	41.97	5.09	224	2118
3-F-an	39.31	4.40	39.56	4.52	209	2124
4-F-an	39.31	4.40	39.03	4.49	215	2117
3-NO_2-an	37.12	4.15	37.11	4.39	213	2123.5
2-Et-an	43.59	5.31	42.48	5.31	192	2124
$(MeO)_2$-an	40.81	5.04	40.99	5.24	171	2124
dmtu	31.93	4.91	32.06	4.90	304	2114
detu[b]	35.22	5.49	35.08	4.74	201	2111
etu[c]	32.1	4.5	32.28	4.58	235	2112
mmtu	30.21	4.61	30.16	4.75	211	2116
taa	31.28	4.53	31.63	4.43	193	2116
$NH_3 \cdot H_2O$[d]	28.28	5.01	28.18	5.09	234	2116 (2036)
NO_2^- [e]	54.70	4.86	54.04	5.11	139	2109
NO_2^- [k]	39.04	6.55	36.44	6.59	150	2132
SCN^- [e]	55.42	4.78	55.03	4.88	201	2116, 2105
CN^- [e]	57.86	4.96	57.17	5.30	170	2143 (CN), 2109 (SCN)
CH_3^- [f]	54.93	5.02	54.64	5.14		2109
$CH_3CH_2^-$ [f]	55.36	5.18	55.07	5.16	185	2106
$CH_3CH_2CH_2^-$ [f]	55.91	5.34	55.82	5.30	190	2101
CN^-, CN^- [e,g]	56.39	4.73	53.88, 54.62[i]	4.68, 5.21[i]	227	2134.5
NO_2^-, NO_2^- [e,h]					205	

[a] Ligand abbreviations are defined in the Experimental Section. [b] N: calcd, 20.54; found, 20.23. [c] N: calcd, 21.8; found, 21.81. Co: calcd, 13.1; found, 13.25. [d] N: calcd, 21.99; found, 22.32. [e] With BPP cation. [f] With TPA cation. [g] Dicyano complex. [h] Dinitro complex. [i] With special instructions. [j] ν_{CN} values in parentheses indicate significantly weaker bands. [k] With $(C_2H_5)_4N^+$ cation.

was a Perkin-Elmer R-12 60-MHz spectrometer. Measurements were also made by using Varian EM-390 and Bruker HFX-90 90-MHz instruments to examine dilute solutions and to determine coupling constants. Elemental analyses were determined by Schwarzkopf Microanalytical Laboratory.

Results and Discussion

Synthesis and Characterization. The analytical results, decomposition temperatures, and thiocyanate ν_{CN} infrared values for all isolated compounds are listed in Table I. All of the complexes with nitrogen and sulfur donors are brown. (There are variations from yellow-brown to dark brown. The $(MeO)_2$-an complex is red-brown.) The alkyl complexes are yellow (methyl, *n*-propyl) or orange-yellow (ethyl). The complexes with NO_2^- and CN^- are orange or red, depending upon the crystal size.

The infrared absorption corresponding to the C–N stretch of thiocyanate (ν_{CN}) is only a qualitative indicator of the thiocyanate's bonding mode in cobaloxime complexes. Norbury and Sinha[44] have reported a small difference in ν_{CN} frequencies for $Co(DH)_2(py)(SCN)$ ($\nu_{CN} = 2118$ cm^{-1}) and $Co(DH)_2(py)(NCS)$ ($\nu_{CN} = 2128$ cm^{-1}). For the complexes examined in this study, a wider range of ν_{CN} values was observed than has been previously reported for cobaloxime complexes.[7]

The preparative methods of Norbury et al.[7] were described as yielding primarily S-bonded complexes. The intermediate complex was, however, isolated as $[Co(DH)_2(NO_2)(NCS)]^-$. During the preparation of complexes with the various nitrogen donors used in this study, it was noted that the solution became yellow-brown upon the addition of ligand. The yellow-brown suspension then became a darker brown, generally within a few minutes. It seems likely that the color change observed is the result of a solvent-promoted isomerization.[28] The change in coordination mode from N to S is the result of a more favorable solvent interaction which facilitates hydrogen bonding.[28] The presence of both linkage isomers is indicated by the asymmetric shape of the IR bands arising from the ν_{CN} exhibited by some of the complexes prepared.

The ν_{CN} frequency trend exhibited by the alkyl complexes is similar to that observed by Crumbliss and Gaus[45] for the ν_{CN} bands of cyano-bridged dicobaloximes containing alkyl groups. This trend was described as resulting from a change in the relative σ-donor strengths of the alkyls as suggested by their σ* values.[46]

Intermolecular hydrogen bonding occurs in the solid state for some of the complexes. Hydrogen bonding is likely to be present in cobaloxime complexes which contain primarily S-bound thiocyanate and are typified by surprisingly low ν_{CN} values. Values which have been previously reported include bands at 2055 cm^{-1} for $Co(DH)_2$(*t*-Bu-py)(SCN)[47] and 1984 cm^{-1} for $Co(DH)(DH_2)(NCS)(SCN)$.[39] These bands are generally weak and occur only in the solid state. For two samples, $Co(DH)_2(NH_3)(SCN) \cdot H_2O$ and $Co(DH)_2$(pip)(SCN), an intense band occurring at 2026 cm^{-1} was observed.

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Table II. Thiocyanate Linkage Isomeric Ratios for Cobaloximes Containing Substituted Pyridine Donors

				K(S/N)		
ligand	pK_a[a]	τ_S[b]	τ_N[b]	this work[c]	Marzilli[d]	Norbury[e]
4-CN-py	1.90	7.34	7.45	1.22	1.44	1:2
3-Cl-py	2.84					1:1
3-Br-py	2.84					1:1
py	5.21	7.45	7.57	1.15	1.35	
3-pic	5.52	7.40	7.53	1.06		2:3
4-*t*-Bu-py	5.99	7.47	7.56	1.01	0.90	
4-ac-py		7.41	7.53	0.88		
4-pic	6.02	7.41	7.53	0.57		2:3
4-NH_2-py	9.11	7.38	7.52	0.63	0.63	not given

[a] Values taken from: Perrin, D. D. "Dissociation Constants of Organic Bases in Aqueous Solution"; Butterworths: London, 1965. [b] Methyl proton resonance of the dimethylglyoximate ligands. [c] 0.05 M in nitrobenzene. [d] 0.05 M in nitrobenzene (from ref 6). [e] $(CD_3)_2SO$ solution, concentration not given.[7]

These low-frequency bands were minimized by altering the preparative route for the ammine complex and recrystallizing the piperidine complex from methanol. Crumbliss and coworkers have also observed[48] a low-frequency band for $Co(DH)_2(pip)(SCN)$ occurring at 2020 cm^{-1}. This band, present in the spectra of solid-state samples, was not present in the solution spectra.

Substituted Pyridine Donors. The proton NMR results for the substituted pyridine complexes examined in this study are listed in Table II. The peak separation for the oxime methyl proton resonances of the two thiocyanate linkage isomers in nitrobenzene[7] is on the order of 2–4 times as great as that reported by Norbury et al. in their study using nonaromatic solvents. This greater separation is the result of the ASIS effect.[49,50] No attempt was made to determine the effect of Co(II) upon the chemical shifts. Because the concentration of Co(II) was roughly equivalent for all the samples examined in this study, it was assumed that all the samples were affected comparably. The results obtained are in good agreement with those of Marzilli et al.[6] The K(S/N) values decrease as the pK_a values increase, although no linear correlation between the two quantities is readily apparent.

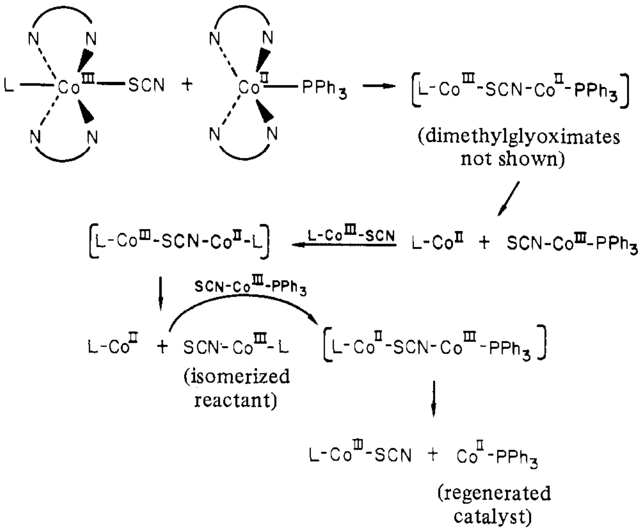
In the absence of Co(II), the isomerization of thiocyanate can be effected via either of the two mechanisms shown in eq 1 and 2, where sol = solvent. Higher dielectric solvents would

$$Co(DH)_2(py)(SCN) \rightarrow Co(DH)_2(py)^+ + SCN^- \rightarrow Co(DH)_2(py)(NCS) \quad (1)$$

$$Co(DH)_2(py)(SCN) + sol \rightarrow Co(DH)_2(py)(sol)^+ + SCN^- \rightarrow Co(DH)_2(py)(NCS) + sol \quad (2)$$

better solvate the ionic species formed, thereby allowing an equilibrium to be reached more rapidly than in low dielectric solvents. Norbury et al.[7] have demonstrated that higher dielectric solvents promote greater amounts of N bonding for $Co(DH)_2(py)(CNS)$. On the basis of these results, it would be difficult to ascertain whether the extent of isomerization is due to solvent-assisted dissociation or a preferential change in bonding mode because of more favorable solvent interactions. In an earlier study, Marzilli[28] found a similar trend between solvent dielectric and K(S/N) for $Co(DH)_2$(*t*-Bu-py)(SCN). Because this prior examination was conducted by using samples with Co(II) present, equilibrium conditions were more rapidly attained, and the extent of isomerization is more clearly the result of solvent control of the bonding mode. The mechanism proposed by Marzilli et al.[6,28] to account for the Co(II) catalysis involves a series of inner-sphere electron-transfer reactions (Scheme I).

Scheme I



On the basis of the results of the solvent studies, the presence of Co(II) appears to be very necessary in order to quickly establish an equilibrium between the two isomers. The rapid isomerization which takes place in the presence of Co(II) (5 min[28]) contrasts sharply with the time required in its absence (3 days).[7] The results emanating from the current study as well as those of Marzilli et al.,[6] where Co(II) was added, clearly demonstrate that the amount of sulfur or nitrogen bonding for thiocyanate is directly a function of the basicity of the trans ligand. That similar results were not observed by Norbury et al.[7] seems to indicate that equilibrium had not been reached.

Phosphorus Donors. Data for cobaloxime complexes containing phosphite and phosphine ligands are given in Table III. These complexes were all generated in situ from $Co(DH)_2$(4-CN-py)(SCN), as in a previous study.[6] The ratios of sulfur to nitrogen bonding [K(S/N)] are compared to the substituent additivity values ($\Sigma\chi$) given by Tolman.[51] These values can be regarded as an inverse measure of the basicity of the phosphites and phosphines. The results obtained demonstrate a rough correlation between K(S/N) and $\Sigma\chi$. Similarly, there appears to be a fairly good relationship between K(S/N) and the pK_a values of the phosphines. This trend parallels that observed for the substituted pyridine donors.

The data collected for both the substituted pyridine donors and the phosphorus donors agree quite well with the results of the study of Marzilli et al.,[6] which strongly suggests that the values of K(S/N) can be related to the trans influence. Costa et al.[16] have described the trans effect of some phosphines in cobaloxime complexes, giving an ordering similar to that presented here. A later study by Allen and Sze[52] produced a similar ordering for the trans influence of phosphines in square-planar complexes. Both studies give evidence that alkylphosphines have higher trans-effect/influences than arylphosphines. Because the sulfur end of thiocyanate has generally been believed to exhibit a stronger trans-effect/influence than the nitrogen end, the observed ordering would seen to follow an antisymbiotic trend.[13] However, recent evidence strongly suggests that, in fact, the nitrogen end possesses a stronger trans-effect/influence in cobaloximes and other octahedral complexes.[21]

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Table III. Thiocyanate Linkage Isomeric Ratios for Cobaloximes Containing Phosphorus Donors

ligand	$\Sigma\chi$[a]	τ_S[b]	τ_N[b]	K(S/N) this study	K(S/N) previous[6]	pK_a
$P(OC_6H_5)_3$	29.1	7.66 (11.35)	7.81 (1.46)	1.08	1.06	
$P(OCH_2)_3CCH_2CH_3$	~30				0.93	
$P(OCH_2CH_2Cl)_3$	28.9	7.44 (1.83)	7.56 (1.15)	0.93		
P(O-allyl)$_3$	23.1	7.47 (1.80)	7.62 (1.25)	0.88		
$P(OCH_3)_3$	23.1	7.45 (1.75)	7.59 (1.25)	0.66	0.79	
P(O-*n*-Bu)$_3$	19.5	7.42 (1.71)	7.57 (1.22)	0.73		
P(O-*i*-Pr)$_3$	18.9	7.49 (1.70)	7.63 (1.00)	0.74	0.65	
$P(CH_2CH_2CN)_3$	21.9	7.31 (1.20)	7.41 (1.15)	2.52		1.44[d]
$P(C_6H_5)_3$	12.9				2.47	2.73[c]
$P(C_6H_5)_2$-*n*-Bu	10.0				1.91	4.99[d]
$P(C_6H_5)_2CH_3$	11.2				1.71	4.6[c]
$P(C_6H_5)_2CH_2CH_3$	10.4	7.40	7.52	1.62		4.91[d]
$P(CH_2CH_3)_3$	5.4	7.56	7.62	1.21		8.69[c]
P-*n*-Bu$_3$	4.2				1.18	8.43[c]

[a] Substituent additivity values given by Tolman.[51] [b] Methyl proton resonance of the dimethylglyoximate ligands, nitrobenzene solution. Numbers in parentheses correspond to values of J_{P-H} (in hertz). [c] Values taken from: Maier, L. In "Organic Phosphorus Compounds"; Kosolapoff, G. M., Maier, L. Eds.; Wiley-Interscience: New York, 1972; Vol. 1, Chapter 1. [d] Calculated by using the equation pK_a = 7.85 − 2.67$\Sigma\sigma^*$, given by: Henderson, W. A.; Streuli, C. A. *J. Am. Chem. Soc.* **1960**, *82*, 5791.

Table IV. Thiocyanate Linkage Isomeric Ratios for Cobaloximes Containing Various Ligands

ligand	τ_S[a]	τ_N[a]	pK_a[b]	K(S/N)
taa[c]	7.39	7.51		1.8
dmtu[c]	7.38	7.51		1.7
detu[c]	7.38	7.49		1.7
etu[c]	7.41	7.51		1.5
2-Cl-an[d]	7.56	7.68	2.65	1.49
4-Br-an	7.46	7.56	3.86	1.38
(MeO)$_2$-an	7.42	7.53		1.29
2-Et-an	7.49	7.58	4.37	1.19
4-Me-an	7.50	7.59	5.08	0.98
5-NO$_2$-iqn	7.38	7.47	3.49	1.77
iqn	7.38	7.50	5.42	0.82
im	7.40	7.53	8.95	0.87
pip	7.34	7.45	11.12	0.84
$CH_3CH_2^-$	7.45	7.74		0.16
$CH_3CH_2CH_2^-$	7.43	7.67		0.15
CH_3^-	7.46	7.69		0.15
NO_2^-	7.40	7.58	3.37	0.10
CN^-	(7.46)[e]	7.50		0.00

[a] Methyl proton resonance of the dimethylglyoximate ligands, nitrobenzene solution. [b] Values taken from: Perrin, D. D. "Dissociation Constants of Organic Bases in Aqueous Solution"; Butterworths: London, 1965. [c] Measured on a 90-MHz NMR spectrometer. [d] Measured on a 90-MHz NMR spectrometer with a 9:1 nitrobenzene to benzene-d_6 solvent mixture. [e] Generated from $[Co(DH)_2(CN)_2]^-$ and $[Co(DH)_2(CNS)_2]^-$.

Table V. ^1H NMR Results for $[Co(DH)_2(CNS)_2]^-$

isomer	this study: oxime ^1H τ[a]	this study: rel intens	previous[36]: oxime ^1H τ[b]	previous[36]: rel intens
S,S	7.25	1	7.61	1
S,N	7.42	1.69	7.58	2
N,N	7.56	1.79	7.55	2

[a] Nitrobenzene solution. Note: because of the aromatic solvent induced shift effect,[49,50] the ordering of the signals is reversed in nitrobenzene from that in nonaromatic solvents. [b] Dimethylformamide solution.

Other Nitrogen Bases. Data for cobaloximes containing other ligands are listed in Table IV. Insufficient solubility precluded the acquisition of satisfactory proton NMR data for the complexes containing aniline and 3-fluoro-, 4-fluoro-, and 3-nitroaniline. For the aniline series, it is again apparent that the ratio of thiocyanate linkage isomers is dependent upon the basicity of the trans ligand. By comparing the K(S/N)'s and pK_a's of all the nitrogen donors, one sees that K(S/N) is not solely dependent upon pK_a. While there is good agreement within a series, it would seen that differences in hybridization of the donor atom and steric requirements of the ligand also play a role in affecting the bonding mode of thiocyanate.

Samuš et al.[18] have investigated the rate of substitution for halides trans to various aniline donors. It was noted that, for these ligands, a linear relationship exists between their pK_a's and Hammett σ values for benzene substituents.[53] The rate of substitution decreased as the pK_a decreased for substituents with negative values of σ (corresponding to electron-donor groups). For substituents with positive values of σ (or electron-withdrawing groups), the rate of substitution increased as the pK_a decreased. When the rate constants for these reactions were plotted against pK_a and σ, the result yielded two different lines. For the plot using Hammett constants, the intersection of these lines corresponded to a σ value slightly more than zero. Such "folding over" would appear to indicate two different mechanisms governing the ligand-substitution processes. No such "folding over" was found from a comparison between the K(S/N) ratios determined here and the pK_a values for the aniline donors used. Ligands with high pK_a values promote N bonding, while those with low pK_a's promote S bonding. The effect of substituent groups is paralleled in the pyridine series.

Alkyls. For alkylcobaloximes (Table IV), a great preference for the nitrogen end of thiocyanate is evident. This is in agreement with the observations of two earlier reports.[23,26] This is somewhat surprising, because the principle of symbiosis[54] would predict sulfur bonding trans to the soft alkyl groups. Some authors have suggested that the alkylcobaloxime moiety is a class b or soft acid.[55,56] Arguments regarding the importance of π bonding[56-58] and electronic and covalent interactions[59] have also been presented.

The hard or class a nature of cobalt(III) has been accepted for some time, and the bonding of thiocyanate has accordingly followed this classification.[13,14] The preference of the metal

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Table VI. Thiocyanate Bonding Patterns[62]

	in the presence of	
	σ-donor ligand	σ-donor and π-acceptor ligand
hard metal center	-NCS	-SCN
soft metal center	-SCN	-NCS

center in (dithiocyanato)cobaloximes for N-bound thiocyanate (Table V) is precisely the behavior expected. The data accumulating for octahedral complexes now discounts the importance of π-bonding arguments regarding the trans influence of ligands.[60] Crumbliss and Gaus[45] have described the bonding between cobalt and carbon in cobaloximes as being almost exclusively σ in nature. This is in agreement with the studies of Hill and Morallee[61] and Toscano and Marzilli,[22] in which alkyls were found to have high trans influences while cyanide (traditionally thought of as having a high trans effect due to π bonding) has a low trans influence.

The bonding of thiocyanate has been summarized[62,63] as in Table VI. Both this generalization and Norbury's calculations[62] appear to be compatible with the conclusion that the sulfur end of SCN^- has the greater trans effect in square-planar complexes while the nitrogen end has the greater trans effect in octahedral complexes.

Other Ligands. Returning to Table IV, it can be seen that S-bound thiocyanates predominate trans to sulfur donors. Sulfur donors are therefore relatively low in trans influence, following the pattern which is becoming more apparent for cobaloximes.[19,21,64] The rough ordering of trans influence based upon $K(S/N)$ is thus as follows: alkyls $\gg$ phosphites $\approx$ pyridines > anilines > phosphines > thioureas. It should not be interpreted that $K(S/N)$ values are an infallible means of assaying the trans influence of ligands in cobaloximes. The low $K(S/N)$ ratios for CN^- and NO_2^- would suggest that they are high in trans influence when, in fact, the opposite is true.[21] Some conflicting data has also been obtained quite recently for complexes with ligands containing group 5A donor atoms.[27] It is apparent, however, that $K(S/N)$ values can provide an empirical measure of the trans influence.

When Crumbliss and Gaus[39] initially prepared $[Co(DH)_2(CN)(CNS)]^-$, they assigned the bonding mode of thiocyanate as being S bound. This was based upon infrared integrated absorption data (both solid state and solution) and the presence of only one ^1H NMR resonance for the oxime methyl group. When this same complex was examined by using ^1H NMR in this study, only one isomer was present, but it now seems more likely that this is the nitrogen-bound isomer. Sufficient quantities for measurement of the S-bound isomer were generated artificially by preparing a solution containing both $[Co(DH)_2(CN)_2]^-$ and $[Co(DH)_2(CNS)_2]^-$. When such a solution was prepared without the addition of Co(II), only two resonances were present. These correspond to $[Co(DH)_2(NCS)(SCN)]^-$ and $[Co(DH)_2(CN)_2]^-$. Following the addition of Co(II), a total of six resonances were observed (Figure 1). The three resonances due to the dithiocyanate complexes could be assigned on the basis of their known frequencies and relative intensities (see Table V). The resonance due to the dicyano complex was assigned by a separate determination. On the basis of these results, it would seem most likely that the τ 7.50 resonance, being more deshielded, is due to the $[Co(DH)_2(CN)(NCS)]^-$ isomer. The ratio of the peak areas for the two cyano–thiocyanato isomers is 0.21 (sulfur to nitrogen). The dominance of nitrogen bonding for this complex is also supported by the solution integrated absorption intensity value reported by Crumbliss and Gaus.[39] Their value (4×10^4 M^{-1} cm^{-2}), while not indicating the complex to be totally N bound, does suggest that a sizable amount of N bonding is present. Because this determination was made in chloroform, a lesser amount of N bonding would be expected than that observed in nitrobenzene solution, on the basis of Marzilli's study of the solvent dependence for these systems.[28]

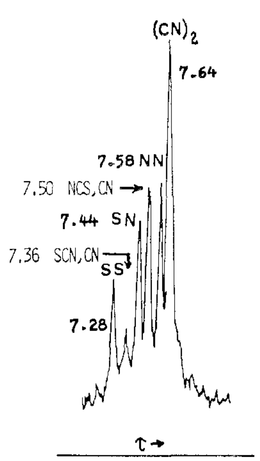

Figure 1. Proton NMR spectrum of the products of the Co(II)-catalyzed reaction between $[Co(DH)_2(CN)_2]^-$ and $[Co(DH)_2(CNS)_2]^-$ (nitrobenzene solution).

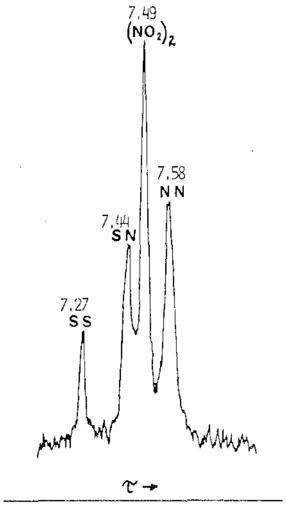

Figure 2. Proton NMR spectrum of the products of the Co(II)-catalyzed reaction between $[Co(DH)_2(NO_2)_2]^-$ and $[Co(DH)_2(CNS)_2]^-$ (nitrobenzene solution).

The observed results for $[Co(DH)_2(CN)(CNS)]^-$ and $[Co(DH)_2(NO_2)(CNS)]^-$ provide an interesting comparison of the relative bridging capability of the thiocyanate, cyanide, and nitro groups. The nitro group is a poor bridging group in cobaloximes, relative to the other two ions. When $[Co(DH)_2(NO_2)_2]^-$ and $[Co(DH)_2(CNS)_2]^-$ were combined in solution with $Co(DH)_2PPh_3$, neither of the isomers of $[Co(DH)_2(NO_2)(CNS)]^-$ were formed (see Figure 2). In order for these isomers to form, it is necessary to have an inner-sphere reduction of $[Co(DH)_2(NO_2)_2]^-$ take place. The required remote attack on the oxygen of the N-bound nitro group is not favorable, due to both steric and electronic factors. This is also demonstrated by the absence of the dinitro complex which might be expected to form when Co(II) is added to $[Co(DH)_2(NO_2)(CNS)]^-$. There has been substantial discussion in the literature concerning the bridging capability of cyanide and thiocyanate cobaloxime complexes.[23,26,45] Remote attack on the thiocyanate is favored sterically because of the

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Table VII. Infrared Data for $[Co(DH)_2(NO_2)(NCS)]^-$ Salts

cation	ν_{CN}(mull), cm^{-1}	ν_{CN}(KBr), cm^{-1}	ISR[a]	ν_{CN}(nitrobenzene), cm^{-1}
Et_4N^+	2132	2130	2.84	2113
BPP^+	2109	2113	1.79	2113

[a] Internal standard ratio calculated according to the method of Hassel and Burmeister,[42] with salicylic acid as the internal standard.

additional atom which is present, and this is further enhanced by the preponderance of nitrogen bonding. Electronically, the sulfur atom of thiocyanate is better suited for attack than the nitrogen of cyanide. Haim[65] has discussed the bridging capability of thiocyanate and the relative ease of attack on the sulfur atom in inner-sphere oxidation–reduction reactions. This is illustrated by the reduction of $[Co(NH_3)_5(SCN)]^{2+}$ by Cr^{2+}, which proceeds by both adjacent and remote attack, and by $[Co(CN)_5]^{3-}$, which proceeds exclusively by adjacent attack. It is therefore quite reasonable that none of the dicyano product was formed from the addition of Co(II) to a solution of $[Co(DH)_2(CN)(NCS)]^-$. The bridging ability of these three ligands in cobaloxime complexes thus decreases in the following order: NCS > CN ≫ NO_2.

The difference between the ν_{CN} value reported by Norbury et al. for $Et_4N[Co(DH)_2(NO_2)(NCS)]$ (ν_{CN} = 2130 cm^{-1}) and that observed in this study for $BPP[Co(DH)_2(NO_2)(NCS)]$ (ν_{CN} = 2109 cm^{-1}) is apparently the result of a solid-state effect caused by changes in crystal packing rather than the result of linkage isomerism. The latter complex was initially isolated as predominantly the S-bound isomer. This is supported by the ν_{CN} frequency of 2099 cm^{-1} observed for this material. A higher frequency shoulder is indicative of some of the N isomer being present. Upon recrystallization from methanol, the material was converted almost totally to the N isomer. A sample of the tetraethylammonium salt was prepared for comparison purposes. The infrared data for both salts are summarized in Table VII. Both salts exhibit solid-state integrated absorption intensity values which correspond to N-bound samples[42] and give the same ν_{CN} frequency in solution. These samples also exhibit very similar ^1H NMR resonances for the oxime methyl groups in the absence of Co(II). The benzyltriphenylphosphonium salt as a solid and both salts in solution exhibit ν_{CN} frequencies which are comparable to those of the alkyl complexes, which also exhibit a great deal of N bonding. It therefore seems likely that the higher frequency ν_{CN} band for the tetraethylammonium salt is the result of a crystal-packing phenomenon.

Hill and Morallee[61] first reported the presence of through-space coupling between the phosphorus of a coordinated phosphine and the oxime methyl protons. Norbury et al.[7] also noted similar coupling for $Co(DH)_2[P(C_6H_5)_3](SCN)$. Phosphorus–proton coupling was observed for all of the phosphites used in this study but could only be resolved for one phosphine (Table III). The larger coupling exhibited by phosphites relative to phosphines is evidently related to the greater amount of s character in the donor orbital of the phosphite phosphorus.[66] The greater coupling for the S isomers relative to the N isomers may be related to differences in the trans influence of the two linkages. The large coupling for the S-bound isomer of the $P(OC_6H_5)_3$ complex is surprising but was verified by measurement at both 60 and 90 MHz.

Aquo(thiocyanato)cobaloximes. Comment on our findings regarding the preparation of $Co(DH)_2(H_2O)(SCN)\cdot H_2O$[34] and $Co(DH)_2(NH_3)(SCN)\cdot H_2O$[33] has been reserved for the latter part of this discussion. The methods used to prepare these complexes are summarized in eq 3 and 4. When these

$$\text{route 1:}\quad H[Co(DH)_2(SCN)_2] \xrightarrow[H_2O]{\text{6 drops of } NH_3(aq)} \tag{3}$$

$$\text{route 2:}\quad Co(DH)_2(NO_2)(H_2O) \xrightarrow[H_2O]{\text{1 equiv of KSCN}} \xrightarrow[\text{cool}]{\text{filter}} \atop \xrightarrow{\text{6 drops of } NH_3(aq)} \tag{4}$$

methods were first reported by Ablov and co-workers, the products were both claimed to be the aquo complex. Norbury and co-workers[7] reported, however, that route 1 gives the ammine complex. They also were critical of Ablov et al.[34] for not analyzing for nitrogen content, a factor which would easily distinguish between the two possible products.

Table VIII. Theoretical and Experimental Elemental Analyses for $Co(DH)_2(CNS)(B)$ (B = H_2O or NH_3) Complexes

	% calcd				% found	
	NH_3	$NH_3\cdot H_2O$	H_2O	$H_2O\cdot H_2O$	route 1	route 2
C	32.98	28.28	32.98	28.28	28.18	28.02
H	3.87	5.01	4.43	4.73	5.09	5.23
N	23.07	21.99	19.23	18.28	22.32	20.99

The results of our attempts to prepare the aquo complex by using route 2 have now cast some doubt upon the feasibility of obtaining the aquo complex by this route as well. Samples were isolated by using both routes. Their analyses, plus theoretical values for the possible hydrated and nonhydrated products which might be expected to form, are listed in Table VIII. The analyses of both of these products are in best agreement with the theoretical values for the ammine monohydrate, although route 1 apparently produces a purer product. Norbury et al.,[7] while describing the necessity for a nitrogen analysis to characterize these compounds, did *not* carry out a nitrogen analysis on the material which they attributed to be the aquo complex. Their elemental analysis for this sample was, in fact, limited to cobalt, which varies only to an insignificant degree between the two species.

When route 2 was initially reported, the use of aqueous ammonia was inferred to make the solution slightly alkaline and lead to the formation of the aquo complex. Therefore, we also attempted to use sodium hydroxide as a substitute. No product was isolated at either of the two concentrations of base used (pH 8 and 10). For route 1, lower amounts of aqueous ammonia were used than those reported[33] for two reasons. When 2 mL of aqueous ammonia was used, substitution for thiocyanate occurred. Lowering the concentration of aqueous ammonia also had the effect of reducing the amount of intermolecular hydrogen bonding indicated by a ν_{CN} band at 2036 cm^{-1}.

Norbury et al.[7] reported values for six different infrared bands for the ammine complex and the complex they reported as the aquo complex. All of these bands exhibited the same frequencies for both samples, including a value of 2116 cm^{-1} for the band arising from the C–N stretch of thiocyanate. The slight difference in the solution ν_{CN} integrated absorption intensities for these complexes may be the result of the different routes of sample preparation employed. Both of our samples also exhibited a ν_{CN} of 2116 cm^{-1} in the solid state.

Hill and Morallee[61] have discussed the manner in which the ^1H NMR chemical shifts for the glyoximate methyl groups reflect changes in the axial ligands. Norbury et al.[7] have reported values for the two samples in question. Both of the samples exhibited only one such band (indicating that only one isomer is present, that being the S-bound thiocyanate), and these were coincident (τ 7.68).

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Table IX. Solvent Effects on Thiocyanate Linkage Isomeric Ratios for Cobaloxime Complexes

ligand	solvent	dielectric constant	τ_S	τ_N	K(S/N)
4-CN-py	benzaldehyde	17	7.48	7.60	1.33
	acetone-d_6	20.7	7.63	7.58	1.34
	benzonitrile	25.2	7.51	7.62	1.21
	nitrobenzene	34.8	7.34	7.45	1.22
detu	benzonitrile	25.2	7.50	7.61	1.9
	nitrobenzene	34.8	7.38	7.49	1.9
4-Br-an	benzonitrile	25.2	7.55	7.67	1.42
	nitrobenzene	34.8	7.46	7.56	1.38

The work of Ablov and Samuš[67] also adds to the confusion regarding the aquo complex. Despite the report[33] of the formation of the aquo complex via route 2 (including a satisfactory nitrogen analysis), this later study stated that the reaction of $Co(DH)_2(NO_2)(SCN)^-$ with aqueous ammonia (albeit in higher concentrations than that cited in the earlier report) gave $Co(DH)_2(NH_3)(SCN)\cdot{}^1/_2H_2O$. On the basis of our experiments and the information reported by Norbury et al.,[7] it appears quite likely that both routes, in fact, lead to the ammine complex.

The ammine complex was too insoluble in nitrobenzene to facilitate measurement of the oxime methyl proton resonance(s). However, signals could be obtained in nitromethane solution. These occurred at τ 7.55 for the N-bound isomer and τ 7.65 for the S-bound isomer. The ratio of the peak areas was 0.53 (sulfur bound to nitrogen bound).

Solvent Effects. The results shown in Table IX indicate that the *K*(S/N) ratio for the 4-cyanopyridine complex responds in a similar manner to changes in solvent dielectric as that previously reported for the pyridine[7] and *tert*-butylpyridine[28] complexes, with regard to both direction and degree, although the lack of differentiation between the benzonitrile and nitrobenzene solvents is somewhat surprising. The relative insensitivity of the cobaloxime *K*(S/N) ratios to changes in solvent dielectric contrasts sharply with the major and more complicated solvent effects on linkage isomeric ratios observed[68,69] for square-planar Pd(II) and Pt(II) thiocyanate complexes. This is undoubtedly due to the greater extent of direct metal–solvent interaction which is possible in the less sterically hindered square-planar complexes, in addition to the solvent–thiocyanate interactions. The results of solution infrared studies indicated that partial ionization took place when the 4-CN-py and detu complexes were dissolved in dimethyl sulfoxide and when the ethyl and propyl complexes were dissolved in benzonitrile.

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Registry No. *trans*-[Co(DH)$_2$(4-CN-py)(SCN)], 57358-21-1; *trans*-[Co(DH)$_2$(4-CN-py)(NCS)], 56954-04-2; *trans*-[Co(DH)$_2$(Py)(SCN)], 30032-62-3; *trans*-[Co(DH)$_2$(py)(NCS)], 30235-61-1; *trans*-[Co(DH)$_2$(3-pic)(SCN)], 30235-63-3; *trans*-[Co(DH)$_2$(3-pic)(NCS)], 73137-69-6; *trans*-[Co(DH)$_2$(4-*t*-Bu-py)(SCN)], 51261-66-6; *trans*-[Co(DH)$_2$(4-*t*-Bu-py)(NCS)], 51261-65-5; *trans*-[Co(DH)$_2$(4-ac-py)(SCN)], 73137-70-9; *trans*-[Co(DH)$_2$(4-ac-py)(NCS)], 73137-71-0; *trans*-[Co(DH)$_2$(4-pic)(SCN)], 30235-64-4; *trans*-[Co(DH)$_2$(4-pic)(NCS)], 15698-22-3; *trans*-[Co(DH)$_2$(4-NH$_2$-py)(SCN)], 57307-43-4; *trans*-[Co(DH)$_2$(4-NH$_2$-py)(NCS)], 56556-16-2; *trans*-[Co(DH)$_2$(P(OC$_6$H$_5$)$_3$)(SCN)], 73137-72-1; *trans*-[Co(DH)$_2$(P(OC$_6$H$_5$)$_3$)(NCS)], 73179-05-2; *trans*-[Co(DH)$_2$(P(OCH$_2$CH$_2$Cl)$_3$)(SCN)], 73137-73-2; *trans*-[Co(DH)$_2$(P(OCH$_2$CH$_2$Cl)$_3$)(NCS)], 73137-74-3; *trans*-[Co(DH)$_2$(P(O-allyl)$_3$)(SCN)], 73137-75-4; *trans*-[Co(DH)$_2$(P(O-allyl)$_3$)(NCS)], 73137-76-5; *trans*-[Co(DH)$_2$(P(OCH$_3$)$_3$)(SCN)], 73137-77-6; *trans*-[Co(DH)$_2$(P(OCH$_3$)$_3$)(NCS)], 73176-11-1; *trans*-[Co(DH)$_2$(P(O-*n*-Bu)$_3$)(SCN)], 73137-78-7; *trans*-[Co(DH)$_2$(P(O-*n*-Bu)$_3$)(NCS)], 73176-12-2; *trans*-[Co(DH)$_2$(P(O-*i*-Pr)$_3$)(SCN)], 73137-79-8; *trans*-[Co(DH)$_2$(P(O-*i*-Pr)$_3$)(NCS)], 73137-80-1; *trans*-[Co(DH)$_2$(P(CH$_2$CH$_2$CN)$_3$)(SCN)], 73137-81-2; *trans*-[Co(DH)$_2$(P(CH$_2$CH$_2$CN)$_3$)(NCS)], 73137-82-3; *trans*-[Co(DH)$_2$(P(C$_6$H$_5$)$_2$CH$_2$CH$_3$)(SCN)], 73137-83-4; *trans*-[Co(DH)$_2$(P(C$_6$H$_5$)$_2$CH$_2$CH$_3$)(NCS)], 73137-84-5; *trans*-[Co(DH)$_2$(P(CH$_2$CH$_3$)$_3$)(SCN)], 73137-85-6; *trans*-[Co(DH)$_2$(P(CH$_2$CH$_3$)$_3$)(NCS)], 73137-86-7; *trans*-[Co(DH)$_2$(taa)(SCN)], 73137-87-8; *trans*-[Co(DH)$_2$(taa)(NCS)], 73137-88-9; *trans*-[Co(DH)$_2$(dmtu)(SCN)], 73137-89-0; *trans*-[Co(DH)$_2$(dmtu)(NCS)], 73137-90-3; *trans*-[Co(DH)$_2$(detu)(SCN)], 73156-83-9; *trans*-[Co(DH)$_2$(detu)(NCS)], 73137-91-4; *trans*-[Co(DH)$_2$(etu)(SCN)], 73137-92-5; *trans*-[Co(DH)$_2$(etu)(NCS)], 73137-93-6; *trans*-[Co(DH)$_2$(2-Cl-an)(SCN)], 73137-94-7; *trans*-[Co(DH)$_2$(2-Cl-an)(NCS)], 73137-95-8; *trans*-[Co(DH)$_2$(4-Br-an)(SCN)], 73137-96-9; *trans*-[Co(DH)$_2$(4-Br-an)(NCS)], 73137-97-0; *trans*-[Co(DH)$_2$((MeO)$_2$-an)(SCN)], 73137-98-1; *trans*-[Co(DH)$_2$((MeO)$_2$-an)(NCS)], 73137-99-2; *trans*-[Co(DH)$_2$(2-Et-an)(SCN)], 73138-00-8; *trans*-[Co(DH)$_2$(2-Et-an)(NCS)], 73138-01-9; *trans*-[Co(DH)$_2$(4-Me-an)(SCN)], 57307-42-3; *trans*-[Co(DH)$_2$(4-Me-an)(NCS)], 73138-02-0; *trans*-[Co(DH)$_2$(5-NO$_2$-iqn)(SCN)], 73138-03-1; *trans*-[Co(DH)$_2$(5-NO$_2$-iqn)(NCS)], 73138-04-2; *trans*-[Co(DH)$_2$(iqn)(SCN)], 73138-05-3; *trans*-[Co(DH)$_2$(iqn)(NCS)], 73138-06-4; *trans*-[Co(DH)$_2$(im)(SCN)], 47379-85-1; *trans*-[Co(DH)$_2$(im)(NCS)], 73138-07-5; *trans*-[Co(DH)$_2$(pip)(SCN)], 57383-07-0; *trans*-[Co(DH)$_2$(pip)(NCS)], 68646-02-6; *trans*-[Co(DH)$_2$(CH$_3$CH$_2$)(SCN)]$^-$, 73138-08-6; *trans*-[Co(DH)$_2$(CH$_3$CH$_2$)(NCS)]$^-$, 73138-09-7; *trans*-[Co(DH)$_2$(CH$_3$CH$_2$CH$_2$)(SCN)]$^-$, 73138-10-0; *trans*-[Co(DH)$_2$(CH$_3$CH$_2$CH$_2$)(NCS)]$^-$, 73138-11-1; *trans*-[Co(DH)$_2$(CH$_3$)(SCN)]$^-$, 49858-71-1; *trans*-[Co(DH)$_2$(CH$_3$)(NCS)]$^-$, 49858-70-0; *trans*-[Co(DH)$_2$(NO$_2$)(SCN)]$^-$, 73138-12-2; *trans*-[Co(DH)$_2$(NO$_2$)(NCS)]$^-$, 30235-65-5; *trans*-[Co(DH)$_2$(CN)(SCN)]$^-$, 56172-79-3; *trans*-[Co(DH)$_2$(CN)(NCS)]$^-$, 53432-70-5; *trans*-[Co(DH)$_2$(SCN)$_2$]$^-$, 47246-90-2; *trans*-[Co(DH)$_2$(SCN)(NCS)]$^-$, 47246-76-4; *trans*-[Co(DH)$_2$(NCS)$_2$]$^-$, 30130-20-2; *trans*-Et$_4$N[Co(DH)$_2$(NO$_2$)(NCS)], 57307-41-2; *trans*-BPP[Co(DH)$_2$(NO$_2$)(NCS)], 73138-13-3; *trans*-[Co(DH)$_2$(NH$_3$)(NCS)], 31826-93-4; *trans*-[Co(DH)$_2$(NH$_3$)(SCN)], 30235-66-6; *trans*-BPP[Co(DH)$_2$(NO$_2$)(SCN)], 73138-14-4; *trans*-TPA[Co(DH)$_2$(NO$_2$)(NCS)], 73138-15-5; *trans*-BPP[Co(DH)$_2$(NCS)$_2$], 73138-16-6; *trans*-BPP[Co(DH)$_2$(CN)(NCS)], 73138-17-7; *trans*-TPA[Co(DH)$_2$(CH$_3$)(NCS)], 43065-08-3; *trans*-TPA[Co(DH)$_2$(CH$_3$CH$_2$)(NCS)], 73138-18-8; *trans*-TPA[Co(DH)$_2$(CH$_3$CH$_2$CH$_2$)(NCS)], 73156-84-0; *trans*-BPP[Co(DH)$_2$(CN)$_2$], 73138-19-9; *trans*-BPP[Co(DH)$_2$(NO$_2$)$_2$], 73138-20-2; *trans*-[Co(DH)$_2$(an)(SCN)], 57326-68-8; *trans*-[Co(DH)$_2$(3-F-an)(SCN)], 73138-21-3; *trans*-[Co(DH)$_2$(4-F-an)(SCN)], 73138-22-4; *trans*-[Co(DH)$_2$(3-NO$_2$-an)(SCN)], 57307-45-6; *trans*-[Co(DH)$_2$(mmtu)(SCN)], 73156-85-1; *trans*-[Co(DH)$_2$(OH$_2$)(SCN)], 54398-30-0.

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