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Carbon-13 Nuclear Magnetic Resonance Study of Coordinated Thiocyanate, Selenocyanate, and Cyanate[1]

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Carbon-13 chemical shifts have been measured for thiocyanate, cyanate, and selenocyanate in a variety of transition-metal complexes. The effects of cation and solvent changes upon the chemical shifts of the ionic pseudohalides have been determined. Changes in hybridization are more important than electron excitation energy changes and substituent changes in determining chemical shifts, for both ionic and complexed species. The ordering of the ions in terms of increasing shielding is $SCN^- < OCN^- < SeCN^-$. The ordering for thiocyanate and selenocyanate in terms of increasing shielding as a function of bonding mode is $M-NCS(Se) < NCS(Se)^- < M-S(Se)CN$. The technique is therefore of considerable utility in the determination of the bonding mode adopted by these groups in solutions of the complexes.

Introduction

The problem of determining the bonding modes adopted by coordinated ambidentate pseudohalide ions such as NCO^-, NCS^-, and $NCSe^-$ has been addressed by the implementation of a wide variety of physical techniques,[2,3] e.g., X-ray diffraction, ESCA, mass spectrometry, and infrared, Raman, electronic, nuclear quadrupole resonance, and nuclear magnetic resonance spectroscopy. These studies of pseudohalide complexes in the solid and gaseous phases, as well as in liquid solution, have met with widely varying degrees of success, and the pros and cons of each technique have been discussed in the reviews cited and in the references contained therein.[2,3]

The NMR techniques employed have ranged from indirect methods, wherein nuclei external to the pseudohalides are probed, to direct utilization of NMR-active nuclei in the pseudohalides themselves. An excellent example of the former is found in the study, by Marzilli et al.,[4] of the Co–SCN/Co–NCS ratios in a series of *trans*-[Co(dimethylglyoximate)$_2$L(thiocyanate)] complexes as a function of the chemical shifts and relative peak areas of the methyl protons of the dimethylglyoximate groups. Most of the work in the latter class has involved ^{14}N NMR studies of thiocyanate complexes,[5] although the technique has been successfully applied to cyanate[6,7] and selenocyanate[8] complexes to a much more limited extent. Prior to our preliminary report[9] of this work, the only published studies involving ^{13}C NMR data for pseudohalides were restricted to organic and ionic species[10] and four chromium– and tungsten–alkyl thiocyanate complexes of the type $M(CO)_5(NCS-R)$.[11] We now wish to report the details of our complete study, which has demonstrated the efficacy of using the ^{13}C chemical shifts of coordinated thiocyanate and selenocyanate as an excellent diagnostic tool for bonding-mode determinations of these groups. The use of the ^{13}C data as a solution probe for pseudohalide complexes promises to be a powerful complement to the recently developed[12] ^{14}N NQR solid-state probe.

Experimental Section

Preparation of Compounds. All chemicals and solvents used were of reagent grade or better. Ethyl thiocyanate, ethyl isothiocyanate, potassium cyanate, $K_2[Hg(SCN)_4]$, and all simple thiocyanate salts were used as obtained commercially. Samples of $K_2[Pt(SCN)_4]$, $K_2[Pd(SCN)_4]$, and $K_2[Zn(NCS)_4]$ were provided by Mr. W. C. Fultz of the University of Delaware. The $K_2[Pd(SCN)_4]$ was converted to the tetra-*n*-butylammonium salt by metathesis in methanol using [*n*-Bu_4N]Cl. The following compounds were prepared according to methods given in the literature (modifications in parentheses): $K[Au(SCN)_2]$,[13] [Au(ethylenethiourea)SCN],[14] $[Co(CN)_5X]^{3-}$,[15,16] $[Co(NH_3)_5X]^{2+}$ ([Co(NH$_3$)$_5$NCS]SO$_4$ was converted to the more soluble acetate salt by suspending it in aqueous solution and treating it with an aqueous solution of barium acetate; the latter was added until the former completely dissolved, whereupon the precipitated barium sulfate was removed by filtration, and the product was isolated by evaporating the solution to dryness),[15,16] [M(pyridine or 4-*tert*-butylpyridine)$_2$(NCO)$_2$] (M = Cd, Zn),[17] $K_2[Hg(SeCN)_4]$,[18] [*n*-Bu$_4$N]NCSe,[18] KSeCN,[19] *trans*-[Co(dimethylglyoximate)$_2$(4-*tert*-butylpyridine)CNS] (allowed to isomerize in solution, giving both linkage isomers, prior to the ^{13}C NMR measurement),[20] [*n*-Bu$_4$N]$_2$[Pd(SeCN)$_4$],[18] [Ni(PR$_3$)$_2$(NCS)$_2$] (R = Et, *n*-butyl; solutions of Ni(NCS)$_2$ in ethanol prepared by metathesis from Ni(NO$_3$)$_2$·6H$_2$O and KSCN, with KNO$_3$ removed by filtration; addition of phosphines carried out under N$_2$),[21] [M(4-*tert*-butylpyridine)$_2$X$_2$] (M = Cd, Zn; X = NCS$^-$, NCSe$^-$; order of addition of reagents altered for NCSe$^-$ complexes: 4-*tert*-butylpyridine added to the aqueous solution of M(NO$_3$)$_2$·6H$_2$O prior to the addition of an acetonitrile (rather than aqueous) solution of KSeCN, thereby minimizing the decomposition of SeCN$^-$),[22] [Et$_4$N]$_2$[M(NCS)$_4$] (M = Zn, Cd),[23] [Cu(P-*n*-Bu$_3$)-SCN]$_4$.[24]

^{13}C NMR Measurements. The ^{13}C chemical shifts were obtained by using a pulsed Bruker HFX-90 spectrometer. The chemical shifts were measured at natural abundance; compounds were therefore chosen with reasonably good solubility in the deuterated solvents used for locking purposes. In the case of ethyl thiocyanate, a few drops of C_6D_6 were added for this reason. A concentration of ca. 0.5 M

Table I. 13C Chemical Shift Data for D_2O Solutions of Various Thiocyanate Salts (35 °C)

compd	δ	compd	δ
$Ca(NCS)_2$	133.5	KNCS	134.0
$Mg(NCS)_2$	133.7	$Ba(NCS)_2$	134.0
NH_4NCS	133.8	LiNCS	134.0

Table II. 13C Chemical Shifts (δ) for Ionic Thiocyanate and Selenocyanate in Various Solvents (35 °C)

solvent	SCN^-	$SeCN^-$
D_2O	134.0[a]	120.7[a]
Me_2SO-d_6	131.0[a]	116.0[b]
acetone-d_6	132.3[b]	117.4[b]
chloroform-d		117.1[b]
benzene-d_6		118.4[b]

[a] With K^+ as cation. [b] With n-Bu_4N^+ as cation.

Table III. 13C Chemical Shift Data for S-Bound Thiocyanate Compounds (35 °C)

compd[a]	solvent	δ	structure
CH_3CH_2SCN	neat	112.1	tetrahedral
$K[Au(SCN)_2]$	Me_2SO-d_6	116.3	linear
Au(etu)SCN	Me_2SO-d_6	116.4	linear
$Co(dmgH)_2(t$-Bu-py)(SCN)	$DCCl_3$	119.5	octahedral
$K_2[Pt(SCN)_4]$	D_2O	121.0	square planar
$K_2[Hg(SCN)_4]$	D_2O	124.8	tetrahedral
$K_3[Co(CN)_5SCN]$	D_2O	127.9	octahedral
$K_2[Pd(SCN)_4]$	D_2O	128.4	square planar
$[Cu(P$-n-$Bu_3)(SCN)]_4$	$DCCl_3$	130.7	cubane-like, with triply bridged sulfur atoms

[a] t-Bu-py = 4-*tert*-butylpyridine; etu = ethylenethiourea; dmgH = monoionized dimethylglyoxime; n-Bu = n-butyl.

in pseudohalide was found to be desirable. Either tetramethylsilane (Me_4Si) or dioxane was used as the internal standard, depending upon whether the solvent medium was organic or aqueous, respectively. The 13C chemical shifts obtained in the latter solutions were converted to the Me_4Si value by adding 67.4 ppm to their values.

Results and Discussion

From the results in Table I for solutions containing ionic SCN^-, it can be inferred that the cation present exerts very little effect on the value of the 13C chemical shift. These values are also in good agreement with a recently reported value for NaSCN in D_2O solution.[25] The chemical shift was also found not to be concentration dependent over the concentration range 0.5–5.0 M.

Chemical shift data for ionic SCN^- and $SeCN^-$ in various deuterated solvents are given in Table II. These results indicate measurable changes in the chemical shifts due to changes in the nature of the solvent. The greatest amount of deshielding occurs in the D_2O solutions. This deshielding seems to be indicative of hydrogen-bonding interactions with the nitrogen end of the ions. Accordingly, the effect of increasing protonation of NCS^- due to increasing HCl concentration was found to be an increase in the thiocyanate 13C chemical shift [δ = 134.2 for $[H^+]/[SCN^-]$ = 0.48, δ = 135.6 for $[H^+]/[SCN^-]$ = 4.8; measured at 35 °C in 50% D_2O–H_2O solution]. As in the case of thiocyanate 14N NMR,[26] the change in chemical shift does not appear to be linearly related to the acid strength.

The chemical shifts for various compounds containing sulfur- and nitrogen-bound linkages are listed in Tables III and IV, respectively. It now seems apparent that the chemical shifts for ionic and S- and N-bound inorganic complexes can be generalized in order of increasing chemical shift from tetramethylsilane:

S-bound < ionic $\leq$ N-bound
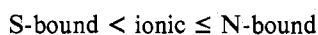
Table IV. 13C Chemical Shifts for N-Bound Thiocyanate Compounds (35 °C)

compd	solvent	δ	structure
CH_3CH_2NCS	$DCCl_3$	128.7	tetrahedral
$[Et_4N]_2[Cd(NCS)_4]$	Me_2SO-d_6	130.2	tetrahedral
$[n$-$Bu_4N]_3[Co(CN)_5(NCS)]$	$DCCl_3$	132.3	octahedral
$K_2[Zn(NCS)_4]$	D_2O	134.1	tetrahedral
$Co(dmgH)_2(t$-Bu-py)(NCS)	$DCCl_3$	137.7	octahedral
$Cd(t$-Bu-py)_2(NCS)_2$	$DCCl_3$	136.7	tetrahedral
$Zn(t$-Bu-py)_2(NCS)_2$	$DCCl_3$	138.7	tetrahedral
$[Co(NH_3)_5(NCS)](C_2H_3O_2)_2$	D_2O	140.5	octahedral
trans-$Ni(P$-n-$Bu_3)_2(NCS)_2$	$DCCl_3$	146.0	square planar
trans-$Ni(PEt_3)_2(NCS)_2$	$DCCl_3$	146.4	square planar

Table V. 13C Chemical Shift Data for Selenocyanate Compounds (35 °C)

| compd	δ D_2O	Me_2SO-d_6	$DCCl_3$
$K_3[Co(CN)_5SeCN]$	109.0		
$K_2[Hg(SeCN)_4]$	113.3		
$[n$-$Bu_4N]_2[Pd(SeCN)_4]$		105.1	
ionic $SeCN^-$	120.7[a]	116.0[b]	117.1[b]
$[n$-$Bu_4N]_3[Co(CN)_5NCSe]$			119.9
$Cd(t$-Bu-py)_2(NCSe)_2$		120.6	
$Zn(t$-Bu-py)_2(NCSe)_2$		122.3	
$[Co(NH_3)_5(NCSe)](ClO_4)_2$		129.7	

[a] K^+ salt. [b] n-Bu_4N^+ salt.

This generalization holds true (with few exceptions) for all the complexes examined when comparisons are made in the same solvent. The small difference in chemical shift observed for $[Zn(NCS)_4]^{2-}$ relative to NCS^- appears to indicate that dissociation or a rapid equilibrium between complexed and dissociated thiocyanate has taken place for this complex. Aqueous studies of this ion made previously with Raman[27] and infrared[28] spectroscopy, however, indicate that it remains intact. There is no such ambiguity regarding the chemical shift for the ion in dimethyl-d_6 sulfoxide (vide infra).

The isomerization of $[Cd(NCS)_4]^{2-}$ in solution has been previously discussed.[3] Conflicting reports have been published regarding this behavior.[27,28] The stability of the ion has been verified by 14N NMR measurements.[26] It is difficult to ascertain from the results obtained here whether isomerization is taking place, although this would explain the low value for the chemical shift.

The results for the $[Cd(t$-Bu-py)_2(NCS)_2]$ complex clearly point out the utility of 13C NMR measurements as a diagnostic tool for bonding-mode determinations. An infrared spectrum of this compound exhibited a ν_{CN} band at 2054 cm^{-1}. This is within the region commonly associated with ionic thiocyanate.[2] The 13C chemical shift for SCN^- in this complex reveals that the ion is coordinated and nitrogen bound.

13C chemical shifts for $SeCN^-$ in some inorganic complexes are given in Table V. When analogous SCN^- and $SeCN^-$ compounds are compared, it can be seen that the latter compounds exhibit chemical shifts which are further upfield. It is also evident that a generalization regarding the mode of selenocyanate coordination and the 13C chemical shift similar to that observed for thiocyanate is relevant here:

Se-bound < ionic < N-bound
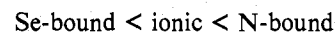
13C chemical shifts for some OCN^- complexes are listed in Table VI. Here, it seems that the ordering of the chemical shifts for N-bound and ionic cyanate is reversed from that observed for thiocyanate and selenocyanate. The cyanate carbon is more shielded than one would be led to expect from a comparison with the results for analogous complexes of the latter two ions. Nitrogen-bound isomers of SCN^- and $SeCN^-$ are deshielded, whereas those of OCN^- are shielded.

Table VI. ^{13}C Chemical Shift Data for Cyanate Compounds (35 °C)

compd	solvent	δ
KNCO	D$_2$O	129.7^a
Cd(t-Bu-py)$_2$(NCO)$_2$	Me$_2$SO-d$_6$	127.9
[Co(NH$_3$)$_5$(NCO)](ClO$_4$)$_2$	Me$_2$SO-d$_6$	127.5
Cd(py)$_2$(NCO)$_2$	Me$_2$SO-d$_6$	127.6
Zn(py)$_2$(NCO)$_2$	Me$_2$SO-d$_6$	~125^b
Zn(t-Bu-py)$_2$(NCO)$_2$	Me$_2$SO-d$_6$	126.3

^{a} From ref 10. ^{b} Obscured by the ^{13}C resonance of the β carbon of pyridine.

Table VII. Chemical Shifts for Aqueous Solutions of NCX$^-$ Ions (35 °C)

|	δ	
ion	^{13}C^a	^{14}N^b
OCN$^-$	+129.7^c	+300^e
SCN$^-$	+134.0^{c,d}	+170^f
SeCN$^-$	+120.7^d	+136^f

^{a} Ppm relative to Me$_4$Si. ^{b} Ppm relative to NO$_3^-$. ^{c} Reference 10. ^{d} This study. ^{e} Reference 6. ^{f} Reference 8.

The dominant factor[29-31] in ^{13}C and ^{14}N NMR, σ_p, expressed in its simplest form is

$$\sigma_p = -\frac{e^2 h^2}{2m^2 c^2 \Delta E}\langle r^{-3}\rangle_{2p}\sum_B Q_{AB}$$

ΔE is the mean excitation energy of ground to excited state electronic transitions, $\langle r^{-3}\rangle_{2p}$ represents atomic 2p-orbital dimensions, and Q_{AB} is a term containing the elements of charge density and bond-order matrix in the MO description of the unperturbed molecule. As the p-orbital size is increased, σ_p becomes smaller and, because of its negative sign, greater shielding occurs. If the energy gap between the highest occupied orbital and lowest unoccupied orbital is reduced, ΔE becomes smaller and deshielding occurs.

Maciel and Beatty[10] have discussed the differences in ^{13}C chemical shifts for OCN$^-$ and SCN$^-$ in terms of changes in hybridization. The results obtained in this study appear to support this assertion. If one compares the ^{13}C chemical shifts for the free ions (given in Table VII) with the estimated resonance contributions,[3,32] it can be seen that SeCN$^-$, which has the greatest contribution of the structure

$$:N\equiv C - \ddot{X}:^-$$
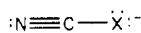
also has the most shielded carbon.

Changes in hybridization apparently offset changes in ΔE (the electron excitation energy). To understand the effect which ΔE can have upon chemical shifts, one need only compare CO$_2$ and CS$_2$. The latter molecule, having a smaller ΔE, has a chemical shift of 193.5 ppm[10] (relative to Me$_4$Si), whereas CO$_2$ has a chemical shift of 124.8 ppm.[33] Thiocyanate does have a smaller ΔE than cyanate;[34] however, there is not a great change in chemical shift. Furthermore, selenocyanate should have an even smaller ΔE but, rather than being less shielded, it is more shielded than the other two ions.

The extent to which hybridization changes have a greater effect than ΔE changes on the chemical shift is also evidenced by a comparison between NCS$^-$ and HNCS. Thiocyanate has a smaller ΔE than HNCS,[34] but, as noted earlier, the effect of adding acid to thiocyanate solutions is seen to deshield the carbon. Nitrogen bonding, in general, deshields the carbon in metal complexes.

A comparison of calculated[35] π-electron atomic charges with chemical shifts also seems to be in order. Comparing the ions collectively does not give a correlation between the observed ^{13}C and ^{14}N chemical shifts for the free ions (Table VII) and

Table VIII. ^{13}C Chemical Shifts (ppm) of Tetrahedral M(t-Bu-py)$_2$(NCX)$_2$ Species (35 °C)

ion	M = Zn	M = Cd	diff
NCO$^-$	127.6	127.9	-0.3
NCS$^-$	138.7	136.7	+2.0
NCSe$^-$	122.3	120.6	+1.7

Table IX. Effect of Solvent upon Coordinated SCN$^-$ (35 °C)

compd	solvent	^{13}C δ
K$_2$[Pd(SCN)$_4$]	D$_2$O	128.4
[n-Bu$_4$N]$_2$[Pd(SCN)$_4$]	Me$_2$SO-d$_6$	119.0
[n-Bu$_4$N]$_2$[Pd(SCN)$_4$]	acetone-d$_6$	117.5
K$_2$[Zn(NCS)$_4$]	D$_2$O	134.1
[Et$_4$N]$_2$[Zn(NCS)$_4$]	Me$_2$SO-d$_6$	134.5

the electron charges (one should really make the comparison with π-charge densities, as yet undetermined). If the ions are treated separately and compared with their protonated forms, one sees that protonation of the nitrogen decreases the π-electron charge on the nitrogen. Sulfur protonation for thiocyanate increases the charge on nitrogen. This agrees with the data collected from ^{14}N chemical shifts.[6-8,26,36] Nitrogen protonation also decreases the charge on carbon for NCS$^-$ while sulfur protonation of thiocyanate increases the charge on carbon. Nitrogen protonation of cyanate increases the charge on carbon. These changes are in line with the chemical shifts observed for carbon. (Protonation of NCSe$^-$ predicts greater charge for the carbon, which disagrees with the observed results.)

The above discussion regarding π charges does not take into account the fact that the thiocyanate carbons in alkyl isothiocyanates are often more shielded[37] than ionic thiocyanate. Carbon–nitrogen bonding in alkyl thiocyanates is apparently stronger than metal–nitrogen bonding in complexes, on the basis of relative bond lengths.[2] It therefore seems justifiable to view the effect in complexes as a perturbation of the metal upon the bonding and hybridization present in thiocyanate. For alkyl compounds, it would appear more proper to view bonding arising from the entire compound. This would act as more than just a perturbation of the bonding present in the ion.

In addition to changes in hybridization and electron excitation energy (ΔE), changes in the polarizability of the X atom would be expected to produce changes in the chemical shift. For a series of methyl halides, the ^{13}C resonance is seen[38] to shift to higher field in the following manner: CH$_3$Cl (24.9 ppm) < CH$_3$Br (10.0 ppm) < CH$_3$I (-20.7 ppm). Substituted acetylenes might be expected to be somewhat similar to NCX$^-$ ions. A comparison of HC≡CSCH$_3$ and HC≡COCH$_3$ shows the α carbon of the former to be at higher field (67.5 ppm) than the latter (88.6 ppm).[39] Similar compounds with halides give the analogous periodic trend.[40] The fact that the ^{13}C chemical shifts of NCO$^-$, NCS$^-$, and NCSe$^-$ do not follow such a periodic trend does not preclude that a contribution to the chemical shift arises from such periodic changes.

It appears that predictable ^{13}C chemical shift changes occur when the metal center is varied within a given geometry. The results for the M(t-Bu-py)$_2$(NCX)$_2$ complexes are summarized in Table VIII. Both thiocyanate and selenocyanate undergo similar increases in shielding when cadmium is the metal center relative to zinc. This would be the expected result, since cadmium is softer than zinc. However, it again seems noteworthy that cyanate behaves differently; coordination to cadmium causes deshielding relative to zinc. This is visible again for the M(py)$_2$(NCO)$_2$ (M = Zn, Cd) complexes (see Table VI).

Preliminary results concerning the effect of solvent upon the ^{13}C chemical shift for coordinated thiocyanate are given

in Table IX. While it is apparent that the solvent does exert an effect upon the chemical shift, further conclusions must be reserved until more data are available. It is very likely that solvent effects will be more difficult to interpret for complexes than for the free ions. In complexes, interactions of the solvent with the metal center and other associated ligands would give some contribution to the observed chemical shifts. Solvent interaction with the exposed d_{z^2} orbitals of palladium may be largely responsible for the greater range of solvent shifts observed for the square-planar $Pd(SCN)_4^{2-}$ relative to the tetrahedral $Zn(NCS)_4^{2-}$. The geometry of the complex would thus be very important when solvent shifts are considered. An added factor is that the solvent interaction with the pseudohalide itself is now limited to that end of the ion which is not coordinated.

Not enough data are presently available to fully ascertain the effect of the metal center upon the ^{13}C chemical shift of the coordinated pseudohalides. In this connection, however, a study[41] concerning the effect of coordination to paramagnetic lanthanide metal centers should be noted.

ESCA has been used to determine the binding energies of the appropriate atomic orbitals for ionic OCN^-, SCN^-, $SeCN^-$, and $TeCN^-$.[42] Basch[43] has suggested a direct correlation between NMR and ESCA measurements. Accordingly, Norbury[3] attempted to correlate the ESCA results with the ^{13}C and ^{14}N chemical shifts for the pseudohalide ions. He noted that there are only small variations in the 1s binding energies for both nitrogen and carbon in all of the XCN^- species. This is in agreement with the relatively small differences in ^{13}C chemical shifts observed for OCN^-, SCN^-, and $SeCN^-$; however, the ^{14}N chemical shifts vary greatly for these ions (see Table VII). In retrospect, it is because σ_p is dependent upon p-orbital size that a comparison between ^{14}N and ^{13}C chemical shifts and their ESCA 1s electron binding energies does not give a uniformly good correlation, and should not be expected to do so.

Registry No. $Ca(NCS)_2$, 2092-16-2; $Mg(NCS)_2$, 306-61-6; NH_4NCS, 1762-95-4; $KNCS$, 333-20-0; $Ba(NCS)_2$, 2092-17-3; $LiNCS$, 556-65-0; $(n\text{-}Bu_4N)NCS$, 3674-54-2; $KNCSe$, 3425-46-5; $(n\text{-}Bu_4N)NCSe$, 7677-15-8; CH_3CH_2SCN, 542-90-5; $K[Au(SCN)_2]$, 40791-29-5; $Au(etu)SCN$, 50589-44-1; $Co(dmgH)_2(t\text{-}Bu\text{-}py)(SCN)$, 51261-66-6; $K_2[Pt(SCN)_4]$, 14244-61-2; $K_2[Hg(SCN)_4]$, 14099-12-8; $K_3[Co(CN)_5SCN]$, 19528-41-7; $K_2[Pd(SCN)_4]$, 14516-47-3; [Cu-$(P\text{-}n\text{-}Bu_3)(SCN)]_4$, 70713-95-0; CH_3CH_2NCS, 542-85-8; $[Et_4N]_2[Cd(NCS)_4]$, 70713-96-1; $[n\text{-}Bu_4N]_3[Co(CN)_5(NCS)]$, 23540-80-9; $K_2[Zn(NCS)_4]$, 15321-17-2; $Co(dmgH)_2(t\text{-}Bu\text{-}py)(NCS)$, 51261-65-5; $Cd(t\text{-}Bu\text{-}py)_2(NCS)_2$, 70713-97-2; $Zn(t\text{-}Bu\text{-}py)_2(NCS)_2$, 70713-98-3; $[Co(NH_3)_5(NCS)](C_2H_3O_2)_2$, 65888-17-7; *trans*-Ni-$(P\text{-}n\text{-}Bu_3)_2(NCS)_2$, 65138-19-4; *trans*-$Ni(PEt_3)_2(NCS)_2$, 15638-53-6; $K_3[Co(CN)_5SeCN]$, 57384-13-1; $K_2[Hg(SeCN)_4]$, 15318-74-8; $[n\text{-}Bu_4N]_2[Pd(SeCN)_4]$, 15639-12-0; $[n\text{-}Bu_4N]_3[Co(CN)_5NCSe]$, 33848-08-7; $Cd(t\text{-}Bu\text{-}py)_2(NCSe)_2$, 70713-99-4; $Zn(t\text{-}Bu\text{-}py)_2$-$(NCSe)_2$, 70714-00-0; $[Co(NH_3)_5(NCSe)](ClO_4)_2$, 57427-34-6; $Cd(t\text{-}Bu\text{-}py)_2(NCO)_2$, 70714-01-1; $[Co(NH_3)_5(NCO)](ClO_4)_2$, 27427-52-7; $Cd(py)_2(NCO)_2$, 32746-62-6; $Zn(py)_2(NCO)_2$, 13878-17-6; $Zn(t\text{-}Bu\text{-}py)_2(NCO)_2$, 70714-02-2.

References and Notes

(1) Based on the Ph.D. dissertation of J.A.K., University of Delaware, June 1979; presented, in part, at the 12th Middle Atlantic Regional Meeting of the American Chemical Society, Hunt Valley, MD, April 5–7, 1978 (see Abstracts, p INOR-10).
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