methyl hydrogen atoms, all of the atoms of the two DMF molecules and two symmetry-related molecules lie in a plane.[13] The largest atom deviation from the four-molecule plane is −0.009 Å for N5 in one DMF and 0.011 Å for C20 in the other. The four DMF molecules have a radial distribution in the plane (Figure 1) and form a quasi-macrocyclic oxygen-donor ligand. The four oxygen atoms form a rectangle with its sides (3.076 (4) and 3.366 (4) Å) relating to the head-to-head and tail-to-tail distribution of the DMF molecules. The dihedral angle between the 4-O DMF and 4-N isoindole planes is −1.4°.

The O–K distances (Figure 3) have a mean value of 2.847 (7) Å and suggest coordination by the DMF. The potassium ions, therefore, are in an eight-coordinate environment and are 1.704 Å from the 4-O DMF plane. The coordination around the potassium ion is distorted cubic and is illustrated in Figure 4. The coordinated O and N atoms are in slightly staggered positions when viewed along the potassium ion chain. The O–K–O angles (68, 72, and 106°) differ from the N–K–N angles and reflect the distortion in the coordination geometry. No unusually close intermolecular DMF contacts are observed.

Structural results for **1**, **2**, and **3** suggest a strong coordination template effect for K_2Pc with both monodentate and sterically more restrictive multidentate oxygen donor ligands. In solution, the coordination template effect is known to enhance ring-closure reactions.[19] Similar enhancement may be possible using the alkali metal phthalocyanines.

In DMF, K_2Pc is a nonelectrolyte (10^{-3} M) and exhibits the single MPc-like Q band (667 nm) associated with a D_{4h} symmetry of the phthalocyanine ring. These observations suggest the presence of the K_2Pc moiety in solution where a species similar to **1** is expected. A similar model for H_2Pc in solution was suggested by Martin and Stillman.[20]

Replacement of the $(DMF)_4$ quasi-macrocycle in **1** with a phthalocyanine dianion is sterically feasible and suggests a possible stacked structural model for the M_2Pc (M = Na, K) compounds, namely, $nM^+(MPc^-)_n$. The structures of these compounds are unkown.

Registry No. $K_2Pc(DMF)_4$, 76081-82-8; K_2Pc, 25047-77-2.

Supplementary Material Available: Tables of the observed and calculated structure factors, the general temperature factor expressions (B_{ij}), the rms amplitudes of thermal vibration, the positional and thermal parameters for the hydrogen atoms and the distance to the attached atom, and weighted least-squares planes (23 pages). Ordering information is given on any current masthead page.

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Organobimetallic Tetrathiocyanates and Their Complexes

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Simple salts of transition and main group elements have been used as Lewis acids frequently. Similarly simple organometallic compounds like $(C_6H_5)_2SnCl_2$ and $(C_6H_5)_3SnCl$ have also been used as Lewis acids. Recently a new class of mixed-metal, bimetallic compounds of general formula $MM'(NCS)_4$ (M = Co, Ni; M′ = Zn, Cd, Hg) have been used as Lewis acids, and a review[1] has recently appeared on this class of bimetallic Lewis acids. We now wish to report the preparation of some organobimetallic, mixed-metal compounds of the type $(NCS)_2Co(NCS)_2Hg_2(C_6H_5)_2$ and $(EtOH)_2(NCS)_2Ni(NCS)_2Hg_2(C_6H_5)_2$. These organobimetallic compounds act as Lewis acids, and the products containing various Lewis bases are reported also.

Experimental Section

Materials and Manipulations. Phenylmercury thiocyanate was prepared by stirring an ethanolic solution of phenylmercury acetate (BDH) with an ethanolic solution of KNCS (BDH) in 1:1 molar ratio. Phenylmercury thiocyanate precipitated immediately, and the solid was isolated by filtration, washed with solvent, recrystallized from acetone, and dried under vacuum. The purity of the compound was determined by elemental analysis, melting point, and infrared spectra.[2] Cobalt and nickel thiocyanates were prepared by reacting their respective nitrates with potassium thiocyanate in ethanol. $Co(NCS)_2 \cdot 2py$ and $Ni(NCS)_2 \cdot 4L$ (L = pyridine, nicotinamide, aniline) were prepared by the method described elsewhere.[3] Dimethyl sulfoxide (Me_2SO), 1,10-phenanthroline (phen), 2,2′-bipyridyl (bpy), tetrahydrofuran (THF), pyridine (py), nicotinamide (Nia), aminopyridine (Amp), dioxane (DIOX), methanol (MeOH), ethanol (EtOH), and acetone were used after purification by known methods.[4] All solvents were purified and dried before use.

Preparation of $(py)_2(NCS)_2Co(NCS)_2Hg_2(C_6H_5)_2$. A 3.32-g sample of $Co(NCS)_2 \cdot 2py$ (1 mmol) was dissolved in 50 mL of ethanol. To this solution was added a suspension of 6.7 g of C_6H_5HgSCN (2 mmol) in 50 mL of ethanol, and the mixture was stirred for 72 h. A pink solid was formed which was filtered, washed with solvent, and dried under vacuum. The compound was recrystallized from Me_2SO.

Preparation of the Lewis acid $(NCS)_2Co(NCS)_2Hg_2(C_6H_5)_2$. This compound was prepared by heating $(py)_2(NCS)_2Co(NCS)_2Hg_2(C_6H_5)_2$ under vacuum at 50–60 °C for about 0.5 h, until the pink color changed to blue; mp 192 °C.

Preparation of $L_2(NCS)_2Co(NCS)_2Hg_2(C_6H_5)_2$ and $[Co(L\text{-}L)_3][C_6HHg(SCN)_2]_2$ (L = py, Nia, Amp, Me_2SO, THF, DIOX; L-L = phen and bpy). All of these complexes were prepared by stirring a suspension of the Lewis acid in ethanol with a solution of the ligand in the some same solvent for 24 h in stoichiometric ratios. The THF, DIOX, and Me_2SO complexes were prepared by stirring the Lewis acid in these solvents. The complexes of bpy and phen were recrystallized from a mixture of ethanol and Me_2SO. The pyridine and nicotinamide complexes melted at 192 and 125 °C, respectively, and rest of the complexes decomposed in the range 170–250 °C.

Preparation of $L_2(NCS)_2Ni(NCS)_2Hg_2(C_6H_5)_2$ (L = MeOH, EtOH, THF, Me_2SO, DIOX). A solution of 1.75 g of $Ni(NCS)_2$ (1 mmol) in 50 mL of methanol was mixed with a solution of 6.7 g (2 mmol) of phenylmercury thiocyanate in 50 mL of acetone, and the mixture was refluxed for 10 h. The methanol complex appeared as a green precipitate, which was filtered and washed with methanol. The compound was recrystallized from Me_2SO and hexane mixture. The remainder of the complexes were prepared similarly by substituting another solvent for methanol. In each case a green solid appeared, which was recrystallized from Me_2SO and hexane mixture. These complexes decomposed in the range 220–260 °C.

Preparation of $L_2(NCS)_2Ni(NCS)_2Hg_2(C_6H_5)_2$ (L = py, Nia, 4-Amp, Ani). $Ni(NCS)_2 \cdot 4L$ (1 mmol) was dissolved in 50 mL of acetone and mixed with a solution of C_6H_5HgSCN (2 mmol) in 50 mL of the same solvent. The reaction mixture was stirred for 2 h, and thereafter 5 mL of methanol was added and stirring continued for 48 h. Violet or bluish green precipitates appeared in each case which were filtered, washed with solvent, recrystallized from a mixture of Me_2SO and hexane, and dried under vacuum. These complexes decomposed in the range 160–230 °C.

Alternatively these complexes were also prepared by refluxing an ethanolic solution of 1 mmol of $(MeOH)_2(NCS)_2Ni(NCS)_2Hg_2(C_6H_5)_2$ with a solution of 2 mmol of the ligands in the same solvent for 15 h.

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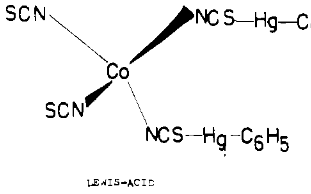

Figure 1.

Preparation of $[Ni(L\text{-}L)_2][C_6H_5Hg(SCN)_2]_2$ (L-L = phen and bpy). These complexes were prepared by mixing an ethanolic suspension of 1 mmol of $(MeOH)_2(NCS)_2Ni(NCS)_2Hg_2(C_6H_5)_2$ and a solution of 2 mmol of the ligands in the same solvent and refluxing the reaction mixture for 24 h. A red or orange compound was formed in each case which was filtered, washed with solvent, recrystallized from Me_2SO and dried under vacuum. These complexes melt at about 160 °C.

Analyses. Sulfur as barium sulfate, mercury as sulfide, cobalt as anthranilate, and nickel as dimethylglyoxime were determined gravimetrically. Nitrogen was estimated by Kjeldahl's semimicro method, and the results are presented in Table I.[5] All the compounds gave satisfactory elemental analysis.

Physical Measurements. Infrared spectra of the complexes were recorded as Nujol mulls or as CsI pellets on a Perkin-Elmer 621 spectrophotometer in the range 4000–200 cm^{-1} and as a polyethylene disk in the range 500–50 cm^{-1} on a Polytech Far-Infrared 30 Fourier spectrophotometer. Electronic spectra were recorded as Nujol mulls or as Me_2SO solutions with use of a Carl-Zeiss DMR-21 spectrophotometer. Magnetic moments have been determined by Gouy's method at room temperature with $CoHg(SCN)_4$ as a standard. The molar conductance of the complexes have been determined in dimethylformamide with use of a Philips conductivity bridge, Model PR-9500, and molecular weights were determined in Me_2SO solution by the cryoscopic method.

Results and Discussion

The complexes of organobimetallic tetrathiocyanates have been divided into two groups.

A. Monomeric Bridged Complexes $L_2(NCS)_2M(NCS)_2Hg_2(C_6H_5)_2$ (M = Co, Ni; L = py, Nia, Amp, Ani, MeOH, EtOH, Me_2SO, THF, DIOX). The complexes are nonconducting in dimethylformamide,[6] and the molecular weights as presented in Table III[5] show that they are monomeric. The infrared spectral band frequencies (Table II[5]) in the ν(C–N) terminal, ν(C–N) bridging, ν(C–S), and ν(NCS) regions, respectively, appear in the ranges 2050–2080, 2130–2170, 690–850, and 420–420 cm^{-1}. They indicate the presence of both bridging and terminal thiocyanates.[7-10]

On being heated under vacuum, the pyridine cobalt complex becomes blue through elimination of the pyridine. The analytical results of the residue corresponds to $(NCS)_2Co(NCS)_2Hg_2(C_6H_5)_2$. This compound melts at 192 °C, and its electronic spectrum shows the presence of bands in the region 16 660 and 8000 cm^{-1} assigned to transitions ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$ (ν_3) and ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$ (ν_2), respectively. These are characteristic of cobalt in a tetrahedral geometry. The magnetic moment value (4.50 μ_B) also supports this configuration. On boiling with water, the Lewis acid $(NCS)_2Co(NCS)_2Hg_2(C_6H_5)_2$ is decomposed and 2 molar equiv of C_6H_5HgSCN are produced. On reaction with the ligands THF, DIOX, Me_2SO, py, Nia, and Amp, it forms the respective adduct. The electronic spectra (Table III[5]) of the cobalt adducts show the presence of three bands in the region 21 000–21 800, 16 600–17 800, and 8500–9100 cm^{-1}. These are respectively assigned to ${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ (ν_3), ${}^4T_{1g} \rightarrow {}^4A_{2g}$ (ν_2), and ${}^4T_{1g} \rightarrow {}^4T_{2g}$ (ν_1) transitions. The spectra of nickel adducts also indicate the presence of three bands in the regions 26 500–28 800, 15 500–16 700, and 9700–10 500 cm^{-1}, which are respectively assigned to ${}^3A_{2g} \rightarrow {}^3A_{1g}(P)$ (ν_3), ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2), and ${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$ (ν_1) transitions. The positions of these bands and spectral parameters derived from them suggest an octahedral geometry around cobalt and nickel. The magnetic moments also support the same geometry.

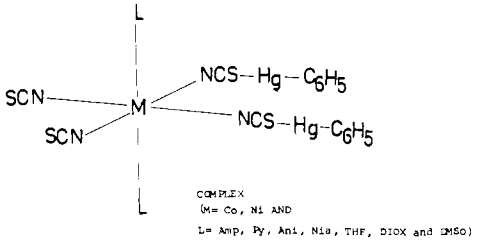

Figure 2.

Table V. Softness Values of Metal Ions and Ligands[a]

ligands	$E_m^{\ddagger}$	ligands	$E_m^{\ddagger}$
methanol	−11.01	aniline	−11.19
ethanol	−10.95	4-aminopyridine	−11.76
dimethyl sulfoxide	−10.87	3-aminopyridine	−11.76
tetrahydrofuran	−10.87	1,10-phenanthroline	−11.81
dioxane	−11.01	2,2'-bipyridyl	−11.44
pyridine	−11.49	NCS (N end)	−12.65
nicotinamide	−13.75	SCN (S end)	−8.22

[a] $E_n^{\ddagger}$ (Co) = −0.38, $E_n^{\ddagger}$ (Ni) = −0.16, and $E_n^{\ddagger}$ (Hg) = −4.99. The softness values of metal ions and of ligands are calculated in the solvent ethanol.

On the basis of these results the following structures (Figures 1 and 2) can be proposed for the Lewis acid and complexes.

The proposed structures are further supported by the following. (1) Far-infrared spectral band frequencies show absence of a Hg–L bond. Hence C_6H_5HgSCN has to retain its original linear structure. This linearity of C_6H_5HgSCN is maintained in the present structure. (2) The structures in Figures 1 and 2 possess C_{2v} symmetry. With assumption of this symmetry the number of infrared-active vibrations for ν(Hg–C), ν(Hg–S), ν(M–NCS), ν(M–L), δ(L–M–L), δ(N–M–N), and δ(S–Hg–C) have been calculated which are presented in Table IV[5] along with the observed number of bands. The calculated and observed number of bands are in good agreement. In the case of Figure 2 local symmetry around M has also been determined for the linkage of L to M in both cis and trans positions. These are respectively C_{2v} and D_{4h}. In the latter only one band corresponding to a M–L stretching model is expected. Since only one band for the M–L stretching mode is observed, the trans L configuration has been adopted. On the basis of previous work[11] the band at 305 cm^{-1} has been assigned to the Co–NCS stretching vibration in the Lewis acid $(NCS)_2Co(NCS)_2Hg_2(C_6H_5)_2$. This band appears in the range 230–260 cm^{-1} when the ligands L are attached to cobalt. The negative shift indicates the change of tetrahedral geometry around cobalt in the Lewis acid to octahedral in the adducts. Clarks and Williams[12] have also observed a similar lowering in ν(Co–NCS) frequency upon changing the coordination number and geometry. Such a change is not observed in the corresponding nickel complexes, because the geometry around nickel in all the monomeric bridged complexes remains octahedral and there is no Lewis acid corresponding to the cobalt species. The Ni–NCS stretching band therefore, remains in the range 235–265 cm^{-1}. (3) Quantitative

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Table VI. Effective Softness Values of Metals

complexes	$E_n^{\ddagger}$(eff) of M	$E_n^{\ddagger}$(eff) of Hg
$CoHg(SCN)_4$	−3.21	−7.83
$(SCN)_2Co(NCS)_2Hg_2(C_6H_5)_2$	−2.87	−7.49
$(MeOH)_2NiHg(SCN)_4$	−2.68	−7.69
$(MeOH)_2(SCN)_2Ni(NCS)_2Hg_2(C_6H_5)_2$	−2.43	−7.32

softness values of the metal ions, ^-NCS, and ^-SCN and various ligands (L) have been calculated by the method reported elsewhere[13,14] and are presented in Table V as $E_n^{\ddagger}$ for metal ions and $E_m^{\ddagger}$ for thiocyanates and ligands. A higher value of difference ΔE_{nm} between the metal ion and the base indicates better match.[15] On the basis of this assumption the ligands (L) prefer linkage to cobalt or nickel. Similarly the N end of thiocyanate shows better match with cobalt and the S end with mercury. Various linkages shown in the proposed structures are consistent with this requirement of the HSAB principle.[16]

B. Ionic Complexes $[Co(phen)_3][C_6H_5Hg(SCN)_2$, $[Co(bpy)_3][C_6H_5Hg(SCN)_2]_2$, $[Ni(phen)_2][C_6H_5Hg(SCN)_2]$, and $[Ni(bpy)_2][C_6H_5Hg(SCN)_2]_2$. These complexes are soluble in Me_2SO and have been crystallized from this solvent. Their molar conductance data as presented in Table III[5] indicate that they are 1:2 electrolytes. The electronic spectra and their spectral parameters and magnetic moments show that cobalt has octahedral coordination geometry and nickel is in a square-planar configuration. The presence of C–N stretching bands in the range 2080–2110 cm^{-1}, C–S stretching in the range 690–725 cm^{-1}, and NCS bending in the range 420–450 cm^{-1} is indicative of thiocyanate linkage through the S atom.

On the basis of these results it can be presumed that the cation consists of a metal ion duly coordinated with the ligand and can be represented by $[Ni(L\text{-}L)_2]^{2+}$ and $[Co(L\text{-}L)_3]^{2+}$. The possible anion is, therefore, $[C_6H_5Hg(SCN)_2]^-$. The coordination number of mercury in the anion is three presumably. Previous workers[17,18] have also reported mercury in tricoordinated state. The cation $[Co(L\text{-}L)_3]^{2+}$ will thus have O_h symmetry and $[Ni(L\text{-}L)_2]^{2+}$ D_{4h} symmetry. The anion $[C_6H_5Hg(SCN)_2]^-$ in both the cases will have C_{2v} symmetry. With assumption of these symmetries the number of infrared-active bands have been calculated and the results are given in Table IV[5] along with the observed number of bands. Both are in good agreement.

Comparison with Corresponding Bimetallic Tetrathiocyanates. (1) Bases like py, Amp, THF, DIOX, and Me_2SO form polymeric bridged complexes with $CoHg(SCN)_4$[19] and monomeric bridged complexes with the organobimetallic tetrathiocyanates. (2) bpy and phen form ionic complexes with $NiHg(SCN)_4\cdot 2H_2O$ and $(C_2H_5OH)_2(NCS)_2Ni(NCS)_2Hg_2(C_6H_5)_2$, but nickel forms octahedral cations with the former and square planar cations with the latter. (3) Soft donors like triphenylphosphine and ethylenethiourea form well-defined compounds of the type $(L)_2Co(NCS)_2Hg(SCN)_2$ (L = triphenylphosphine and ethylenethiourea) with $MHg(SCN)_4$.[20] The corresponding organobimetallic compounds do not react with these ligands. The calculation of effective softness values[14] of cobalt and nickel as presented in Table VI in both types of Lewis acid show that these metal ions become harder in the organobimetallic compounds. The increase in hardness might be the possible reason for their inactivity toward soft bases. (4) The organobimetallic compounds are comparatively more soluble in common organic solvents, and their molecular weights can be determined. Most of these complexes are crystalline, and the cobalt Lewis acid has a sharp melting point. The corresponding bimetallic tetrathiocyanates are generally insoluble solids, which have a broad decomposition range. (5) Singh and Srivastava[14] have reported a new method known as "matching constant" for deriving comparative stability in a set of related complexes. The results of matching constant calculations as presented in Table IV[5] indicate that the complexes of organobimetallic compounds are more stable than the complexes of bimetallic tetrathiocyanates. This appears reasonable because the THF complexes of bimetallic tetrathiocyanates lose their THF at room temperature, whereas the corresponding complex does not lose THF even on mild heating.

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Registry No. $(py)_2(SCN)_2Co(NCS)_2Hg_2(C_6H_5)_2$, 77462-25-0; $(SCN)_2Co(NCS)_2Hg_2(C_6H_5)_2$, 77462-24-9; $(Nia)_2(SCN)_2Co(NCS)_2Hg_2(C_6H_5)_2$, 77462-23-8; $(3\text{-}Amp)_2(SCN)_2Co(NCS)_2Hg_2(C_6H_5)_2$, 77462-22-7; $(4\text{-}Amp)_2(SCN)_2Co(NCS)_2Hg_2(C_6H_5)_2$, 77462-21-6; $(Me_2SO)_2(SCN)_2Co(NCS)_2Hg_2(C_6H_5)_2$, 77462-20-5; $(THF)_2(SCN)_2Co(NCS)_2Hg_2(C_6H_5)_2$, 77462-19-2; $(DIOX)_2(SCN)_2Co(NCS)_2Hg_2(C_6H_5)_2$, 77462-18-1; $(phen)_3(SCN)_2Co(NCS)_2Hg_2(C_6H_5)_2$, 77462-17-0; $(bpy)_3(SCN)_2Co(NCS)_2Hg_2(C_6H_5)_2$, 77462-16-9; $(MeOH)_2(SCN)_2Ni(NCS)_2Hg_2(C_6H_5)_2$, 77462-15-8; $(EtOH)_2(SCN)_2Ni(NCS)_2Hg_2(C_6H_5)_2$, 77462-14-7; $(Me_2SO)_2(SCN)_2Ni(NCS)_2Hg_2(C_6H_5)_2$, 77462-13-6; $(THF)_2(SCN)_2Ni(NCS)_2Hg_2(C_6H_5)_2$, 77482-01-0; $(DIOX)_2(SCN)_2Ni(NCS)_2Hg_2(C_6H_5)_2$, 77462-12-5; $(py)_2(SCN)_2Ni(NCS)_2Hg_2(C_6H_5)_2$, 77462-11-4; $(Nia)_2(SCN)_2Ni(NCS)_2Hg_2(C_6H_5)_2$, 77462-10-3; $(Ani)_2(SCN)_2Ni(NCS)Hg_2(C_6H_5)_2$, 77462-09-0; $(4\text{-}Amp)_2(SCN)_2Ni(NCS)_2Hg_2(C_6H_5)_2$, 77462-08-9; $(phen)_2(SCN)_2Ni(NCS)_2Hg_2(C_6H_5)_2$, 77519-67-6; $(bpy)_2(SCN)_2Ni(NCS)_2Hg_2(C_6H_5)_2$, 77519-45-0; $Co(NCS)_2\cdot 2py$, 15613-11-3; C_6H_5HgSCN, 16751-55-6; $Ni(NCS)_2\cdot 4py$, 14724-08-4; $Ni(NCS)_2\cdot 4Nia$, 63313-22-4; $Ni(NCS)_2\cdot 4(4\text{-}Amp)$, 72804-72-9; $Ni(NCS)_2\cdot 4Ani$, 14324-74-4.

Supplementary Material Available: Tables I–IV (analytical and IR and electronic spectral data) and the spectral traces of the IR (4000–200 cm^{-1}) and far-IR (450–50 cm^{-1}) for $(4\text{-}Amp)_2(SCN)_2Ni(NCS)_2Hg_2(C_6H_5)_2$ (6 pages). Ordering information is given on any current masthead page.

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Oxidative-Addition Reaction of Bis(diphenylphosphino)methane with $Ru_3(CO)_{12}$. Formation of a "Capped" Phosphinidene Triruthenium Carbonyl Cluster

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Transition-metal clusters are the focus of considerable attention in view of catalysis.[1] However, their possible degradation under potentially interesting reaction conditions is an obstacle to proving cluster catalysis. This led several groups

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