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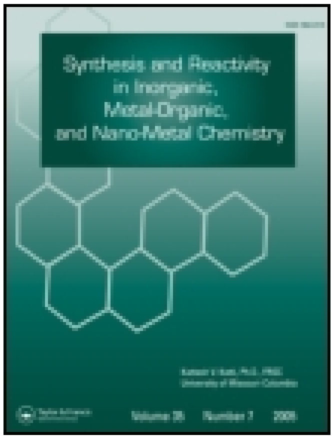

Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt19

SYNTHESIS AND ELECTRICAL PROPERTIES OF SOME NEW HETEROBIMETALLIC COORDINATION POLYMERS $MPb(SCN)_4$ (M = Co, Ni) AND THEIR REACTION PRODUCTS WITH LEWIS BASES

Nanhai Singh [a] & Vinay Kumar Singh [a]
[a] Department of Chemistry, Faculty of Science , Banaras Hindu University , Varanasi, 221 005, India

Published online: 15 Feb 2007.

To cite this article: Nanhai Singh & Vinay Kumar Singh (2001) SYNTHESIS AND ELECTRICAL PROPERTIES OF SOME NEW HETEROBIMETALLIC COORDINATION POLYMERS $MPb(SCN)_4$ (M = Co, Ni) AND THEIR REACTION PRODUCTS WITH LEWIS BASES, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 31:10, 1743-1757, DOI: 10.1081/SIM-100108259

To link to this article: http://dx.doi.org/10.1081/SIM-100108259

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SYNTH. REACT. INORG. MET.-ORG. CHEM., 31(10), 1743–1757 (2001)

SYNTHESIS AND ELECTRICAL PROPERTIES OF SOME NEW HETEROBIMETALLIC COORDINATION POLYMERS $MPb(SCN)_4$ (M = Co, Ni) AND THEIR REACTION PRODUCTS WITH LEWIS BASES

Nanhai Singh* **and Vinay Kumar Singh**

Department of Chemistry, Faculty of Science,
Banaras Hindu University, Varanasi 221 005, India

ABSTRACT

This paper describes a study of the electrical conducting behaviour of some new heterobimetallics of the composition $MPb(SCN)_4$ (M = Co(II), Ni(II)) and their Lewis base products of the forms $MPb(SCN)_4L_2$ (L = pyridine (py) or triphenylphosphine (PPh_3)) and $[M(phen)_3][Pb(SCN)_4]$ (M = Co(II) or Ni(II); phen = 1,10-phenanthroline). The properties of these were investigated by using spectroscopic (IR, UV-Visible) methods as well as powder XRD and conductivity techniques. The IR spectra showed the bridging nature of SCN^- in $MPb(SCN)_4$ and $MPb(SCN)_4(py)_2$, both terminal and bridging SCN^- in $NiPb(SCN)_4(PPh_3)_2$ and only terminal SCN^- groups in $[M(phen)_3][Pb(SCN)_4]$. The magnetic data and electronic absorptions are also compatible with these proposed

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*Corresponding author. E-mail: nsingh@banaras.ernet.in

arrangements. Based on these studies, polymeric, monomeric and ionic structures have been proposed for these compounds. All of the compounds exhibited solid state σ_{rt} values in the 10^{-12} to $10^{-6}\,S\,cm^{-1}$ range, and all showed semiconductivity from 303 to 363 K. A notable increase in conductivity, 10^2–10^3 increase, at higher temperatures suggested some type of phase transition/packing equilibrium changes which produce effective M...S/Pb...S/S...S intermolecular interactions in $NiPb(SCN)_4$ and $[M(phen)_3][Pb(SCN)_4]$.

INTRODUCTION

The field of inorganic complex-based conductors is now very well advanced[1–5]. Many charge transfer salts[1–3, 6–10] of TTF (tetrathiafulvalene) and BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) with anionic complexes of: thiocyanate (SCN^-) or dithiolates of transition metals e.g., $K(BEDT\text{-}TTF)_2[Cu(NCS)_2]$, $(BEDT\text{-}TTF)_2X[M(SCN)_4]$ ($X = NH_4^+$, Tl^+, Na^+, K^+ or Rb^+; M = Co(II), Zn(II), Cd(II) or Hg(II)), $[(BEDT\text{-}TTF)_n][Re_2(NCS)_{10}]\cdot C_6H_5CN/CH_2Cl_2$ (n = 2 or 3), $[(BEDT\text{-}TTF)_2][Cr(NCS)_4(NH_3)_2]$, $[TTF][Ni(dmit)_2]_2$ ($dmit^{2-}$ = 1, 3-dithiol-2-thione-4, 5-dithiolate) and heterobimetallic complexes $M[Ag_2(ecda)_2]$[4], $[NBu_4^n]_2[M(mnt)_2Cu_4I_4]$[5] (M = Ni, Pd or Pt; $ecda^{2-}$ = 1-ethoxycarbonyl-1-cyanoethylene-2,2-dithiolate; mnt^{2-} = maleonitriledithiolate), showed semiconducting, metallic or superconducting behaviour. In these systems, the conducting properties have been mainly attributed to S...S/M...S intermolecular contacts present in the solid-state. Also, some related complexes are important MOCVD precursors for semiconducting materials[11].

Since the introduction of $CoHg(SCN)_4$ as a well known Gouy standard in magnetic measurements, an extensive amount of work has been done on homo- and heteropolynuclear thiocyanato complexes[12–18]. This extremely versatile ambidentate ligand is capable of bridging two similar or dissimilar metals providing diverse and unusual[15] electronic properties that depend on the bonding arrangements of the S and N donors. For example, the tetranuclear complex, $[Cu(oxpn)Ni(\mu\text{-}NCS)H_2O(tmen)]_2(ClO_4)_2$ (oxpn = N,N′-bis(3-aminopropyl)oxamide, tmen = N,N,N′,N′-tetramethylethylenediamine) possess a Cu-Ni bond as well as a Cu-SCN-Ni grouping, and it displays ferro- and antiferromagnetic alternations[16]. While, in the case of $[Cu_2Pb(SCN)_3L_3]$ (L = 2-dimethylaminoethanol)[16], where dimerisation has occurred through bridging NCS^- groups the hexanuclear units so formed are linked by Pb...S interactions between adjacent units to form layered supramolecular assemblies.

Keeping with the well-pronounced conducting properties of the chalcogen-rich ligand complexes and: their applications to material science, we herein present the syntheses, characterizations and solid state conductivities of some new heterobimetallic coordination polymers, $CoPb(SCN)_4$ and $NiPb(SCN)_4$ and their reaction products with Lewis bases.

EXPERIMENTAL

Materials

Nickel nitrate, potassium thiocyanate, pyridine (py) and 1,10-phenanthroline (phen), all British Drug House products, were manufactured by E. Merck India Ltd., and triphenylphosphine (PPh_3) was obtained from Aldrich Chemical Co., Inc. These were used without further purification. KSCN was dried before use. The starting compounds $Co(NCS)_2$ or $Ni(NCS)_2$ were prepared by reacting equimolar-quantities of $Co(NO_3)_2$ or $Ni(NO_3)_2$ and KSCN in ethanol while $Pb(SCN)_2$ was obtained by reacting $Pb(NO_3)_2$ and KSCN in a 1:2 molar ratio in water according to the known methods[19,20]. Ethanol was dried over calcium oxide and distilled before use. All experiments were carried out in air.

Synthesis of the Heterobimetallic Complexes

$CoPb(SCN)_4$ and $NiPb(SCN)_4$

A suspension of 2 mmol of $Co(NCS)_2$ (0.350 g) or $Ni(NCS)_2$ (0.349 g) and $Pb(SCN)_2$ (0.646 g) in dichloromethane (25 mL) was stirred at room temperature (30 °C) for about 72 h. Alternatively, these were also prepared by refluxing equimolar quantities of the constituent metal thiocyanates in dichloromethane. The resulting bluish-green/yellowish-green powders were filtered out and dried *in vacuo* over $CaCl_2$; the yields were, 0.976 g (98%) for $CoPb(SCN)_4$ and 0.915 g (92%) for $NiPb(SCN)_4$.

$MPb(SCN)_4L_2$ and $MPb(SCN)_4(phen)_3$ ($M = Co(II)$) or Ni(II);
$L = py$ or PPh_3)

A solution of py (0.2 mL, ~2 mmol), PPh_3 (0.524 g, 2 mmol) or phen (0.595 g, 3 mmol) in dichloromethane (5 mL), was added to 20 mL of a suspension of 1 mmol of $CoPb(SCN)_4$ (0.498 g) or $NiPb(SCN)_4$ (0.497 g) in the same solvent. In each case, the reaction mixture was stirred for about

24 h. The resulting solid products, were filtered and dried *in vacuo* over $CaCl_2$; the yields were 0.636 g (97%) for M = Co(II), L = py; 0.955 g (92%) for M = Co(II), L = phen; 0.950 g (93%) for M = Ni(II), L = PPh_3 0.965 g (93%) for M = Ni(II), L = phen; 0.623 g (95%) for M = Ni(II), L = py.

Analysis and Physical Measurements

Microanalyses of C, H and N were performed on a model 1108 Carlo Erba elemental analyser at the Central Drug Research Institute, Lucknow. Sulfur was determined as $BaSO_4$. Conductivities were measured in 10^{-3} M DMSO solutions on a WTW Leitfahigkeitsmesser conductivity-meter, and the melting points were obtained in open capillaries and are uncorrected. Powder XRD patterns of the samples were recorded at room temperature on a Rigaku (Japan) Rotaflex M/S diffractometer, using Cu-Kα radiation at $\lambda = 1.5405$ Å. IR spectra (4000–400 cm^{-1}) were recorded in KBr pellets with a JASCO FTIR-5300 spectrophotometer. Electronic spectra were recorded on a Cary-14 or 23 spectrophotometer as Nujol mulls by following the techniques of Lee[21]. Room temperature magnetic susceptibilities were measured on a Cahn Faraday electrobalance using $CoHg(SCN)_4$ as the standard. The diamagnetic corrections were evaluated from Pascal's constants.

RESULTS AND DISCUSSION

The elemental analyses (Table I) are consistent with the formation of heterobimetallic thiocyanato complexes of the type, $MPb(SCN)_4$, $MPb(SCN)_4L_2$ and $MPb(SCN)_4(phen)_3$ (M = Co(II) or Ni(II); L = py or PPh_3), and these have been characterized by magnetic susceptibility measurements, IR and UV-Visible spectroscopy and powder XRD analysis. These solids are stable at room temperature, and decompose in the 195–295 °C temperature range. In the case of the py adducts, there are colour changes above 70 °C. The compounds are insoluble in water and common organic solvents like ethanol, methanol and acetone, but they are soluble in DMSO and DMF, with characteristic changes in their colours *i.e.*, from bluish-green to pink for the cobalt and yellowish-green/sky-blue to green for the nickel complexes. The electrical conductivities of $> 66.6\,\Omega^{-1}\,cm^2\,mole^{-1}$ in 10^{-3} M DMSO solution are close to those expected for 2:2 electrolytes[22], and this is consistent with their substantial decomposition as shown below.

Table I. Analytical Data and General Properties of the Complexes

Complexes Empirical Formula F.W.	Colour Yield (%)	Dec. p. (°C)	% Found (Calculated)				Magnetic Moment μ_{eff} (BM)	$\Lambda_m(\Omega^{-1}\ cm^2\ mole^{-1})$ in 10^{-3} M DMSO	σ^a_{rt}, S cm^{-1} (Ea^b, eV)
			C	H	N	S			
CoPb(SCN)$_4$ $C_4N_4S_4CoPb$ 498.1	Greenish-blue 0.976 g (98)	290–295	9.5 (9.6)	–	11.1 (11.2)	25.2 (25.6)	4.35	90.82	4.46×10^{-9} (0.6580)
CoPb(SCN)$_4$(py)$_2$ $C_{14}H_{10}N_6S_4CoPb$ 456.3	Pink 0.636 g (97)	> 70	25.3 (25.6)	1.5 (1.5)	12.7 (12.8)	18.9 (19.5)	4.9	54.49	5.60×10^{-6} (–)
CoPb(SCN)$_4$(phen)$_3$ $C_{40}H_{24}N_{10}S_4CoPb$ 1038.1	Pink 0.955 g (92)	205–210	46.1 (46.2)	2.2 (2.3)	13.4 (13.4)	12.2 (12.3)	4.96	44.80	8.11×10^{-12} (0.7658)
NiPb(SCN)$_4$ $C_4N_4S_4NiPb$ 497.9	Yellowish-green 0.915 g (92)	285–290	9.6 (9.6)	–	11.2 (11.2)	25.1 (25.7)	3.30	66.60	3.42×10^{-6} (0.6567)
NiPb(SCN)$_4$(PPh$_3$)$_2$ $C_{40}H_{30}N_4S_4P_2NiPb$ 1021.8	Orange 0.950 g (93)	210–215	47.1 (46.9)	2.8 (2.9)	5.3 (5.4)	12.4 (12.5)	2.73	84.77	2.39×10^{-8} (0.3752)
NiPb(SCN)$_4$(phen)$_3$ $C_{40}H_{24}N_{10}S_4NiPb$ 1037.9	Sky Blue 0.965 g (93)	195–200	46.2 (46.2)	2.3 (2.3)	13.4 (13.4)	12.1 (12.3)	3.3	42.38	3.52×10^{-10} (0.7180)
NiPb(SCN)$_4$(py)$_2$ $C_{14}H_{10}N_6S_4NiPb$ 656.1	Light green 0.623 g (95)	> 70	25.6 (25.6)	1.4 (1.5)	12.7 (12.8)	19.4 (19.5)	3.21	33.30	1.11×10^{-6} (0.0683)

σ^a_{rt} =Room temperature conductivity.

$E_a{}^b$ = Activation energy in electron volt.

$$\mathrm{MPb(SCN)_4 \rightleftharpoons [M(DMSO)_6]^{2+} + [Pb(SCN)_4]^{2-}} \tag{1}$$

However, in the case of the phen complexes the colour is unchanged on dissolution. Their Λ_M values of 44.80 and 42.38 $\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{mole}^{-1}$ [Co-Pb, Ni-Pb] are somewhat low for 2:2 electrolytes, and this is consistent with extensive ion-pairing in DMSO, a solvent of relatively low dielectric constant, and the presence of highly charged species as shown in the following equilibria:

$$\begin{aligned}&\mathrm{MPb(SCN)_4(phen)_3 \rightleftharpoons [M(phen)_3]^{2+}}\\&\quad \mathrm{+ [Pb(SCN)_4]^{2-} \rightleftharpoons [M(phen)_3]^{2+}[Pb(SCN)_4]^{2-}}\end{aligned} \tag{2}$$

Magnetic and Spectroscopic Studies

In the IR spectra of the compounds, the bands are highly characteristic[12–14,23] for bridging and terminal, coordinated SCN^- ligands (Table II). A very strong band at 2100 cm^{-1} and a shoulder at 2170 cm^{-1} due to $\nu(C{\equiv}N)$ in $CoPb(SCN)_4$ and $NiPb(SCN)_4$, correspond to bridging SCN^- groups. $NiPb(SCN)_4(PPh_3)_2$ exhibits distinct bands at 2170 and 2090 cm^{-1}, which are indicative of both bridging and terminal SCN^- groups. In the case of their py adducts, the occurrence of bands at around 2100 cm^{-1} is consistent with the conclusion that the coordination of py does not affect the bridging mode of these bimetallic tetrathiocyanates whereas their trisphen groups rupture the bridges between the two metal centres resulting in only terminal SCN^- groups as indicated by the IR bands near 2080 cm^{-1}. All of the compounds show weak absorptions around 760 and 850 cm^{-1} characteristic of the ν(C-S) frequency of coordinated SCN^- moieties. Absorptions at around 430 and 640 cm^{-1} indicate mono/bidentate coordination of the py and phen groups. In the far-IR region (Fig. 1), $NiPb(SCN)_4{\cdot}2PPh_3$ consists of bands at 307 and 206 cm^{-1} which correspond to ν(Ni-NCS) and ν(Pb-SCN) modes[12,24], respectively. The bands at 175 and 154 cm^{-1} are characteristic[24] of ν(Ni-P) vibrations. These IR bands, and the established[25] bulkiness of the ligand PPh_3 suggest a monomeric formulation of this compound.

Both the effective magnetic moments and the electronic spectral bands (Table I and II) are compatible with a symmetrical tetrahedral geometry about the Co(II) centre in $CoPb(SCN)_4$ and octahedral geometries[26] around Co(II) in its py and phen complexes. However, the features of the absorptions for the two nitrogen-containing base adducts are somewhat different because of changes in the environment about the metal centre. The dia-

Table II. Infrared and UV-Visible Spectral Data of the Bimetallic Complexes

	IR (cm^{-1}) as KBr Pellete (Assignment)			UV-Vis
Complexes	ν(C≡N)	ν(C-S)	Coordinated py, phen Bands	λ_{Max}nm (in Nujol Mull)
$CoPb(SCN)_4$	2100 s	780 w	–	615, 690 sh, 1375
$CoPb(SCN)_4(py)_2$	2100 s	760 m	630 w, 450 w	610, 1080
		790 w		
$CoPb(SCN)_4(phen)_3$	2070 s	760 w	640 w, 440 w	500, 1050
	2050 m	790 m		
$NiPb(SCN)_4$	2100 s	770 m	–	450, 650, 1050
	2170 m			
$NiPb(SCN)_4(PPh_3)_2$	2090 s	750 s	–	450
	2170 m	785 w		
$NiPb(SCN)_4(phen)_3$	2080 s	760 w	635 w, 440 w	550,770, 925, 1175
	2050 sh	790 m		
$NiPb(SCN)_4(py)_2$	2080 s	765 m	630 m, 440 w	600, 975
	2050 sh	760 m		

s = strong, m = medium, w = weak, sh = shoulder.

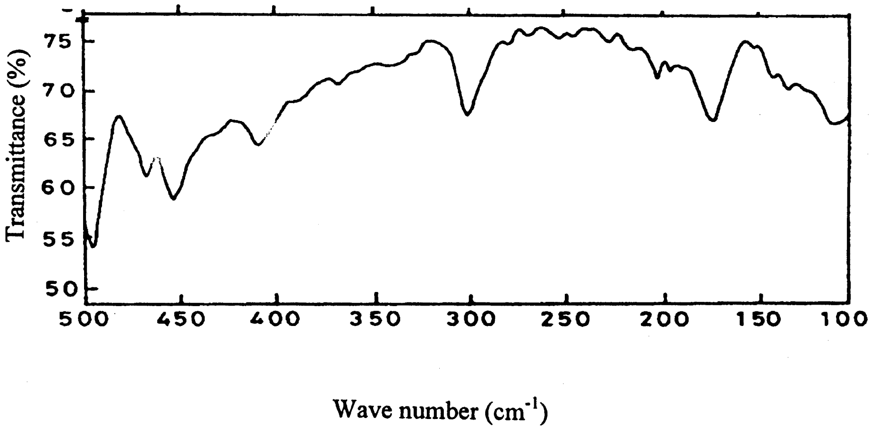


Figure 1. Far-IR (500–100 cm^{-1}) spectrum of NiPb(SCN)$_4$(PPh$_3$)$_2$.

magnetic behaviour together with the UV-Visible bands are suggestive of square-planar geometry[26,27] about Ni(II) in the orange coloured NiPb(SCN)$_4$(PPh$_3$)$_2$. Magnetic moment values and electronic spectral bands suggest octahedral geometries[26] for nickel(II) in NiPb(SCN)$_4$ and its base adducts with py and phen. In the case of NiPb(SCN)$_4$, octahedral geometry around Ni(II) is possibly achieved, probably because of Ni...S axial interactions in a layered polymeric array of this compound.

Powder X-Ray Diffraction Spectra

Powder X-ray diffraction patterns show the crystalline nature of the compounds. A comparison of powder patterns (Fig. 2) of the starting compounds, e.g., Co(NCS)$_2$, Ni(NCS)$_2$ and Pb(SCN)$_2$ with the bimetallic complexes CoPb(SCN)$_4$ and NiPb(SCN)$_4$, clearly reveals that the heterobimetallics are new species and not mixtures of the constituent metal thiocyanates. Further, the powder patterns, which are largely dependent on the lattice geometries of the crystal structures, show that the compounds are not isostructural.

Inspite of all efforts, the general insolubility of these compounds prevented their crystallization. Based on the foregoing studies and known structures[12], a polymeric structure for MPb(SCN)$_4$ and MPb(SCN)$_4$(py)$_2$, a monomeric structure for NiPb(SCN)$_4$(PPh$_3$)$_2$, and an ionic structure for MPb(SCN)$_4$(phen)$_3$ (Fig. 3) have been proposed.

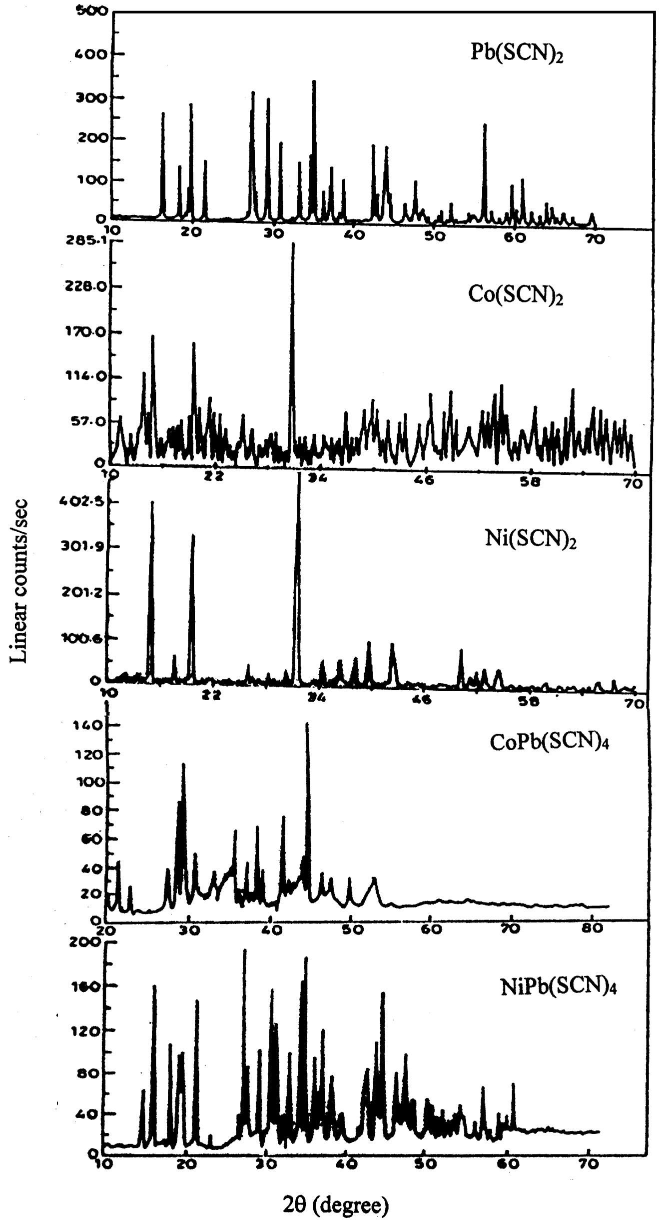
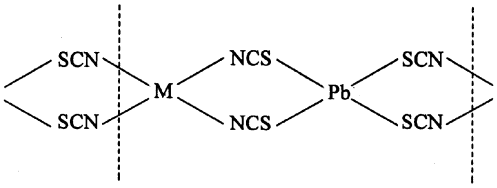
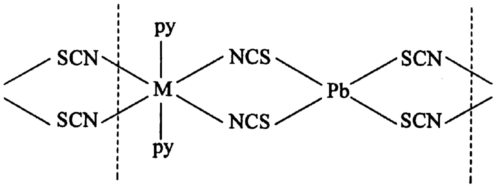


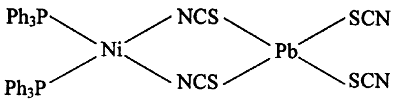
Figure 2. Powder XRD patterns of the complexes.



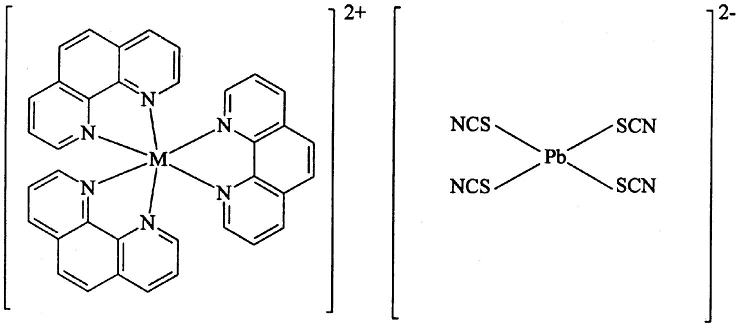
MPb(SCN)$_4$



MPb(SCN)$_4$(py)$_2$



MPb(SCN)$_4$(PPh$_3$)$_2$



[M(phen)$_3$]$^{2+}$ [Pb(SCN)$_4$]$^{2-}$
M = Co(II) or Ni(II)

Figure 3. Proposed structures for the complexes.

Electrical Conductivity

The temperature (303–363 K) dependence of the compressed pellet conductivities were studied by using a conventional two-probe technique on a Keithley 236 source unit. The pellets were prepared at a load of 20 KN; silver paint was used to adhere the contacts to the pellet surfaces. A sequence of increasing voltages were passed through the leads while the current across the current leads was measured. Resistance was calculated from the slope of I/V curves. Resistivities were calculated from the resistance measurements using known dimensions of the sample pellets. All of the compounds show σ_{rt} values in the 10^{-12} to 10^{-6} S cm^{-1} range, and they are semiconductors (Fig. 4) over the above temperature range. Except for $CoPb(SCN)_4(py)_2$ where a deviation from a straight line is observed, the remaining compounds provide plots of log σ versus T^{-1} that are nearly linear which produce activation energies, Ea, in the 0.06 to 0.76 eV range. In the cases of $NiPb(SCN)_4$ and the complex bimetallic salts $[M(phen)_3][Pb(SCN)_4]$, a remarkable increase in conductivity is observed, i.e., on the order of 10^2–10^3, with increasing temperature which may be the result of some type of phase transformations or changes in packing equilibria. In the majority of cases, the temperature dependence of the conductivity is reproducible, but in the case of the py adducts the behaviour is almost similar to their parent Lewis acids, $CoPb(SCN)_4$ and $NiPb(SCN)_4$, which strongly suggests that at higher temperatures the py molecules are lost. The lower conductivities of these materials, as compared to anionic thiocyanato compounds[6–10] with dominant S…S intermolecular stacking containing BEDT-TTF as counter cation, may be attributed to weaker S…S, Pb…S and M…S intermolecular contacts[16]. However, in the absence of single crystal X-ray structures, definite conclusions about the conductivity mechanisms cannot be drawn.

CONCLUSION

All of the heterobimetallic complexes reported herein exhibit semiconducting properties, and in a few cases remarkable increases in conductivity at higher temperatures which are attributed to effective intermolecular stackings. In conclusion, unlike $CoHg(SCN)_4$ and $NiHg(SCN)_4$, which can be prepared in water as well as in methanol, ethanol or acetone by reaction of the constituent metal thiocyanates or by replacement of K^+ in $K_2[Hg(SCN)_4]$ by Co(II)/Ni(II), analogous bimetallic compounds containing Pb(II) could not be synthesized in either of the polar solvents, instead they could be synthesized by reaction of monometallic

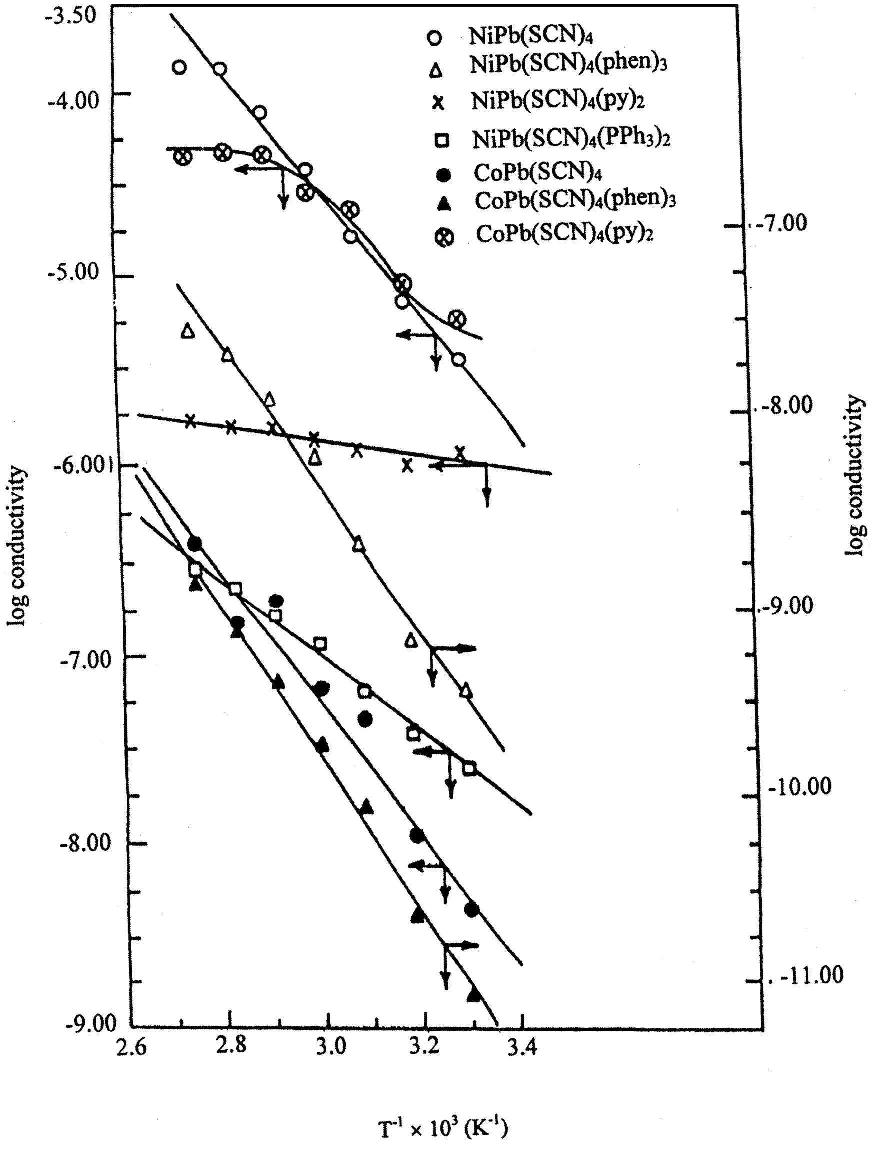


Figure 4. Temperature dependence of the electrical conductivities of the complexes.

thiocyanates in highly non-polar solvents like CH_2Cl_2/CCl_4 in which they are insoluble. This difference in synthetic methodology may be attributed to the borderline character of both Co(II)/Ni(II) and Pb(II) in contrast to the soft behaviour of Hg(II) in accordance with Pearson's HSAB principle[28]. Due to the same reasons, the strength of bridging in $CoPb(SCN)_4$/ $NiPb(SCN)_4$ is weaker than that of the $CoHg(SCN)_4$, coordination polymer. It is observed that the use of non-polar solvents greatly influence the hard/soft nature of metal ions and promotes even less favourable interactions to occur.

ACKNOWLEDGMENT

One of the authors, Vinay Kumar Singh, acknowledges Banaras Hindu University for financial assistance in the form of a scholarship.

REFERENCES

1. Cassoux, P.; Valade, L. Molecular Inorganic Superconductors. In *Inorganic Materials*; 2nd Edn.; Bruce, D.W., O'Hare, D., Eds., Chapter 1, John Wiley: NewYork, 1996; 1–64.
2. Cassoux, P.; Valade, L.; Kobayashi, H.; Kobayaslu, A.; Clark, R.A.; Underhill, A.E. Molecular Metals and Superconductors Derived from Complexes of 1,3-Dithiol-2-thione-4,5-dithiolate (dmit). Coord. Chem. Rev. **1991**, *110*, 115–160.
3. Zhu, D.B.; Xing, X.C.; Wu, P.J.; Wang, P.; Zhang, D.M.; Yang, D.L. New Organic Conductors Based on Bis(1,1-dicyanoethylene-2,2-dithiolato). Transition Metal. Synth. Met. **1991**, *42*, 2541–2546.
4. Singh, N.; Gupta, S. Complex Salt and Heterobimetallic Complexes Derived from Bis(1-ethoxycarbonyl-1-cyanoethylene-2,2-dithiolato) Diargentate(I) ion: Preparation, Spectroscopic Investigation and Electrical Conductance Properties. Polyhedron **1999**, *18*, 1265–1271.
5. Sugimoto, K.; Kuroda-Sowa, T.; Maekawa, M.; Munakata, M.A. Novel Eight-Membered Cu_4I_4 Ring Supported by Sulfur Atoms of an $M(mnt)_2$ Moiety. Syntheses and Crystal Structures of $(NBu^n{}_4)_2$ $[M(mnt)_2Cu_4I_4]$ (M = Ni, Pd, Pt; mnt = 1,2-Dicyano-1,2-ethylenedithiolato) With Doubly-Bridged One-Dimentional Chain Structures. Chem. Commun. **1999**, 455–456.
6. Urayama, H.; Yamochi, H.; Saito, G.; Sato, S.; Kawamoto, A.; Tanaka, J.; Mori, T.; Maruyama, Y.; Inokuchi, H. Crystal Structures of

Organic Superconductors, $(BEDT\text{-}TTF)_2$ $Cu(NCS)_2$ at 298 K and 104 K. Chem. Lett. **1988**, 463–466.

7. Oshima, M.; Mori, K.; Saito, G.; Oshima, K. Crystal Structures and Electrical Properties of BEDT-TTF Salts of Mercury(II) Thiocyanate with and without K ion. Chem. Lett. **1989**, 1159–1162.
8. Mori, H.; Hirabayashi, I.; Tanaka, S.; Mori, T.; Maruyama, Y. Organic Conductors With Three-Component System Containing Co, Zn and Cd Based Upon BEDT-TTF. Synth. Met. **1995**, *70*, 789–790.
9. Kepert, C.J.; Kurmoo, M.; Day, P. Bis(ethylenedithio)tetrathiafulvalene(BEDT-TTF) Charge Transfer Salts of $Re_2(NCS)_{10}{}^{n-}$ (n = 2,3). Inorg. Chem. **1997**, *36*, 1128–1135.
10. Kepert, C.J.; Kurmoo, M.; Trutter, M.R.; Day, P. Quasi-One-Dimensional Bis(ethylenedithio)tetrathiafulvalene Charge-Transfer Salts With Paramagnetic Group 6 Anions. J. Chem. Soc., Dalton Trans. **1997**, 607–613.
11. Bochmann, M.; Webb, K.J. Sterically Hindered Thiolato, Selenolato and Tellurolato Complexes of Mercury(II). J Chem. Soc., Dalton Trans. **1991**, 2325–2329.
12. Forster, D.; Goodgame, D.M.L. Infrared Spectra (400–200 cm^{-1}) of some Thiocyanate and Isothiocyanate Complexes.; Isothiocyanato Complexes of Nickel(II) and Copper(II). Inorg. Chem. **1965**, *4*, 715–718; 823–829.
13. Singh, P.P. Bimetallic Tetrathiocyanates and Selenocyanates as Lewis Acids. Coord. Chem. Rev. **1980**, *32*, 33–65.
14. Baily, R.A.; Kozak, S.L.; Michelsen, T.W.; Mills, W.N. Infrared Spectra of Complexes of the Thiocyanate and Related Ions. Coord. Chem. Rev. **1971**, *6*, 407–445.
15. Ribas, J.; Diaz, C.; Costa, R.; Tercero, J.; Solans, X.; Font-Bardia, M.; Stoeckli-Evans, H. Synthesis and Magnetic Properties of Four New $(Cu\text{-}Ni)_2$ Tetranuclear Complexes of General Formula $[Cu(oxpn)Ni(\mu\text{-}NCS)(H_2O)(aa)]_2(X)_2$ (oxpn = N,N′-Bis(3-aminopropyl)oxamide; aa = Bidentate Amine; X = ClO_4 or $PF_6{}^-$). Ferro and Antiferromagnetic Alternation. Inorg. Chem. **1998**, *37*, 233–239.
16. Kovbasyuk, L.A.; Vassilyeva, O.Y.; Kokozay, V.N.; Linert, W.; Reedijk, J.; Skelton, B.W.; Oliver, A.G. A Thiocyanato-bridged Layer Structure Composed of Symmetrical, Dithiocyanato (N,S)-bridged Dimers of Heterotrinuclear Alkoxo-bridged Cu_2Pb Units; Synthesis from Zerovalent Copper, Structural, Spectroscopic and Magnetic Studies. J. Chem. Soc., Dalton Trans. **1998**, 2735–2738.
17. Zhang, H.; Wang, X.; Zhang, K.; Teo, B.K. Crystal Engineering in $[(12)C_4)_2Na][Cd(SCN)_3]$: First Example of an Anionic Cadmium Thiocyanate Coordination Solid with a Sandwich $[(12C_4)_2Na]^+$ Cation

as Spacer/Controller Resulting in a Hexagonal Arrangement of Antiparallel Zig-Zag $[Cd(SCN)_3^-]_\infty$. Chains. Inorg. Chem. **1998**, *37*, 3490–3496.

18. Navarro, J.A.R.; Romero, M.A.; Salas, J.M.; Quiros, M.; Tiekink, E.R.T. First Example of Equatorial-Equatorial Disposition of End-to-End Thiocyanate Bridges in a Polynuclear Copper (II) Complex and Its Relation to the Very Efficient Transmission of the Magnetic Interaction. Inorg. Chem. **1997**, *36*, 4988–4991.
19. Brauer, G. In *Hand Book of Preparative Inorganic Chemistry*; 2nd Edn.; Academic Press: New York, London, 1963; Vol. 1, 769.
20. Singh, P.P.; Yadav, S.P.; Sharma, S.B. Synthesis and Structural Studies of Some Tetrathiocyanate and Tetraselenocyanate Binuclear Mixed-Metal Complexes. Aust. J. Chem. **1977**, *30*, 1921.
21. Lee, R.H.; Griswold, E.; Kleinberg, J. Studies on the Stepwise Controlled Decompostion of 2,2-Bipyridine Complexes of Cobalt(II) & Nickel(II) Chlorides. Inorg. Chem. **1964**, *3*, 1278–1283.
22. Geary, W.J. The Use of Conductivity Measurement in Organic Solvents for the Characterization of Coordination Compounds. Coord. Chem. Rev. **1971**, *7*, 81–122.
23. Nakamoto, K.; Thiocyanato and Other Pseudohalogeno Complexes. In *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; 4th Edn., Wiley Inter Science: New York, 1986; 282.
24. Makhija, R.; Pazdernik, L.; Rivest, R. Cobalt(II) Mercury Tetrathiocyanate Complexes With Lewis Bases. Can. J. Chem. **1973**, *51*, 438–447.
25. Tolman, C.A. Steric Effects of Phosphorus Ligands in Organometallic Chemistry and Homogeneous Catalysis. Chem. Rev. **1977**, *77*, 313–348.
26. Lever, A.B.P. Electronic Spectra of d^n Ions. In *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1984; 479–507.
27. Pecile, C. Infrared Studies of Planar and Tetrahedral Inorganic Thiocyanates. Inorg. Chem. **1966**, *5*, 210–214.
28. Pearson, R.G. Recent Advances in the Concept of Hard and Soft Acids and Bases. J. Chem. Ed. **1987**, *64*, 561–567.

Received July 25, 2000
Accepted August 21, 2001

Referee I: K. Moedritzer
Referee II: B. N. Storhoff