ter Größe, aber deutlicher – wenn auch verwackelter – Kristallstruktur, die in Form eines Tridymit- bzw. Quarzgitters angenommen wird. EUCKEN [10] hingegen sieht Molekülassoziationen $(H_2O)_m$ mit m-Werten zwischen zwei und acht für die Sonderstellung des Wassers als ausschlaggebend an. Bei vorliegender Elektronenbeugungsuntersuchung ergaben sich einerseits Gründe, die quasikristallinen Molekülschwärme *unbestimmter* Größe nach BERNAL und FOWLER durch EUCKENS Assoziationskomplexe zu ersetzen. Andererseits konnte in diesen *kleinsten Bereichen* eine ganz beträchtliche Ordnung nachgewiesen werden, die weit über das für Flüssigkeiten übliche Maß hinausgeht und näherungsweise mit Teilbereichen des Tridymitgitters übereinstimmt. Somit will es scheinen, als wäre der Widerspruch zwischen der Vorstellung einer quasikristallinen Wasserstruktur und der von Assoziationskomplexen beseitigt, indem nachgewiesen werden konnte, daß die EUCKENschen Assoziationskomplexe ganz die Eigenschaften von quasikristallinen Molekülschwärmen besitzen und somit mit diesen identifiziert werden können.

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The Infra-red Spectrum of the Thyocyanate Group in the Pyridine Complexes of Cu(II), Ni(II) and Co(II)

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The compounds $Co(Py)_4Cl_2$, $Co(Py)_2Cl_2$, $Cu(Py)_2(NCS)_2$, $Co(Py)_4(NCS)_2$ and $Ni(Py)_4(NCS)_2$ were synthesized and their I.R. spectra recorded. The assignment of the vibrational frequencies is given with reference to the crystal structure of these compounds.

Co(II), Ni(II) and Cu(II) can be determined gravimetrically by precipitation with pyridine and thiocyanate as $Co(Py)_4(NCS)_2$ [1,2], $Ni(Py)_4(NCS)_2$ [3] and $Cu(Py)_2(NCS)_2$ [4]. These compounds are stable in vacuum for a few hours, but are readily decomposed by heat. The infra-red spectra of these compounds and their decomposition products were recorded. To help in the identification of the pyridine bands of the complexes, $Co(Py)_4Cl_2$ and $Co(Py)_2Cl_2$ were synthesized and their infra-red spectra recorded. The powder-diffraction and infra-red data for $Co(Py)_4(NCS)_2$ and $Ni(Py)_4(NCS)_2$ show that these compounds are isomorphous.

General

The "free" NCS^- ion has three fundamental vibrational modes, all of which are active in the infrared. The C – N stretching mode (ν_1) occurs at ca. 2060 cm^{-1}, the doubly degenerate bending mode (ν_2) at ca. 480 cm^{-1} and the C – S stretching mode (ν_3) at ca. 750 cm^{-1} (see refs. [5–7]).

Several possibilities arise when the NCS^- ion is part of a complex:

1) The ion is *outside* the co-ordination sphere [in complexes of the type $(MX_n)(NCS)_m$]. The vibrational frequencies of the NCS^- ion would then approximate those of the "free" ion.

2) The ion is part of the complex and is coordinated through the nitrogen atom. Two possibilities arise here for the C – N and C – S stretching vibrations in complexes of the type $MX_4(NCS)_2$ and $MX_2(NCS)_2$, depending on whether the NCS^- ions are *cis* or *trans* to each other (or otherwise expressed, on whether the angle between the two NCS groups is 180° or smaller than 180°).

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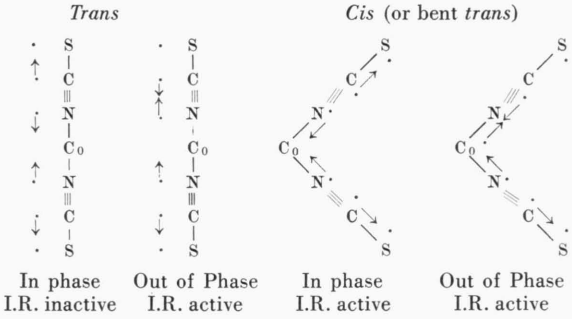

The *Cis* (or bent *trans*) configuration would lead, in principle, to the doubling of the C – N and C – S stretching vibrations as compared with the *trans* configuration and would probably cause the broadening of the bands of the *Cis*-compounds. The same applies when the ion is co-ordinated only through the S-atom.

3) A combination of (a) and (b), i. e. complexes of the type $[MX_2Y(NCS)](NCS)$ (Y is an ionic ligand), would also lead to the doubling of the bands[8].

4) Co-ordination through *both* the N and the S atoms would lead to a rise in frequency of the N – C and C – S modes. This situation arises in the blue compound $CoHg(SCN)_4$ where S co-ordinates with Hg and N with Co[9–11]. ν_1 is shifted to ca. $2140\ cm^{-1}$ and ν_3 to ca. $790\ cm^{-1}$ in the compounds $MHg(SCN)_4$, where $M^{++} = Co^{++}$, Cd^{++}, Zn^{++}, Fe^{++}, Ni^{++} and Cu^{++}[6, 12].

Experimental

1) $Co(Py)_4(NCS)_2$ was prepared according to Spacu and Dick[1, 2]. The precipitate was found to consist of thin light-red needles.

calculated: $\%C = 53.74$; $\%H = 4.1$;
found : $\%C = 53.80$; $\%H = 4.2$.

2) $Co(Py)_4(NCS)_2$, when heated for 1 hour at 104 °C loses two molecules of pyridine and turns mauve, forming $Co(Py)_2(NCS)_2$. A thermogravimetric analysis shows that the onset of the reaction is at ca. 65 °C. This reaction is slow to complete and is followed by the loss of the last two pyridine molecules. The infra-red spectra of partially decomposed and decomposed samples of $Co(Py)_2(NCS)_2$ show that the two pyridines are lost successively. The reaction scheme is probably:

$$Co(Py)_4(NCS)_2 \xrightarrow[104°\,C]{1\,hr} Co(Py)_2(NCS)_2 \xrightarrow{115°} Co(Py)(NCS)_2 \xrightarrow{115°} Co(NCS)_2 .$$

The final product is a yellowish-brown substance, probably $Co(NCS)_2$.

calculated: $\%C = 13.12$;
found : $\%C = 14.1$.

α-$Co(Py)_2(NCS)_2$ was also synthesized by boiling an alcoholic solution of $Co(Py)_4(NCS)_2$ and allowing to crystallize[13].

3) The light-blue compound $Ni(Py)_4(NCS)_2$ was synthesized according to Spacu and Dick[3].

calculated: $\%C = 53.76$; $\%H = 4.1$;
found : $\%C = 53.84$; $\%H = 3.9$.

4) $Cu(Py)_2(NCS)_2$ was synthesized from $CuSO_4$, KCNS and pyridine[4]. The resulting compound was green in colour.

5) $Co(Py)_4Cl_2$ was synthesized by heating anhydrous $CoCl_2$ with anhydrous pyridine[14] and allowing to crystallize out. The compound was obtained in the form of light-red crystals.

calculated: $\%C = 53.83$; $\%H = 4.56$;
found : $\%C = 52.55$; $\%H = 4.55$.

It was found that this light-red compound rapidly turns blue on exposure to air and eventually becomes white. After heating $Co(Py)_4Cl_2$ for 10 hours at 115 °C it yielded a mauve product which has the composition $Co(Py)Cl_2$.

calculated: $\%C = 28.87$; $\%H = 2.4$;
found : $\%C = 28.67$; $\%H = 2.3$.

The composition of the two intermediate decomposition products was not determined.

The infra-red spectra of the above substances were recorded on a Perkin-Elmer Model 21 Spectro-

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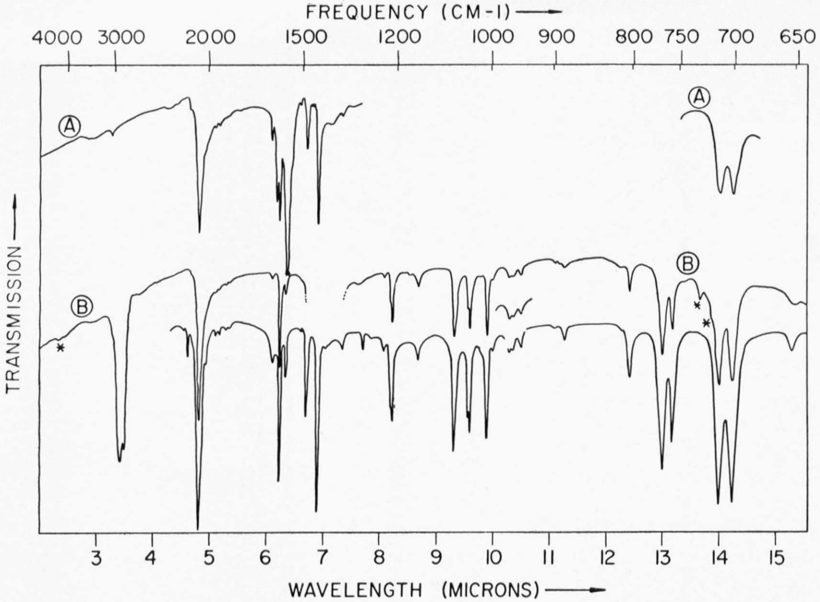

Fig. 1. The infra-red spectrum of $Co(Py)_4(NCS)_2$. A. Mull in hexachlorobutadiene; B. Mull in vaseline; C. Suspension in KBr (1.0 mg/300 mg KBr; 1 mm thick). * Bands due to mulling-agent.

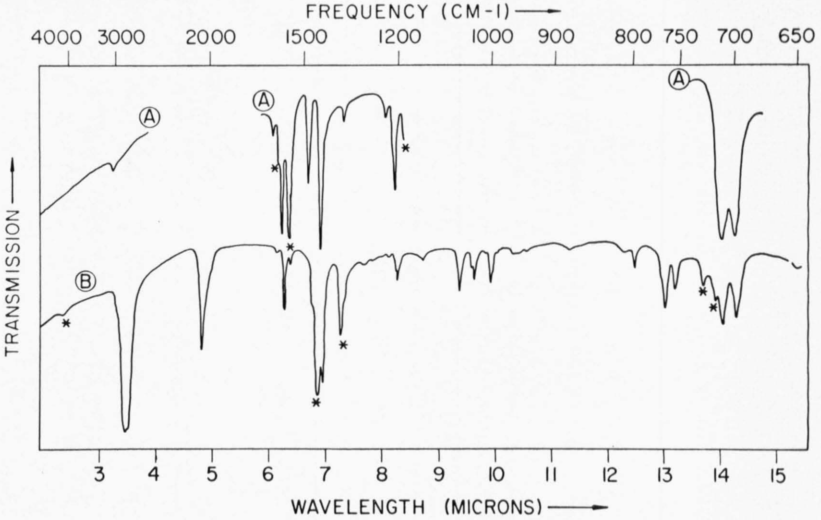

Fig. 2. The infra-red spectrum of $Ni(Py)_4(NCS)_2$. A, B see Fig. 1. * Bands due to mulling-agent (the bands at ca. 3.5 μ in B are due to the vaseline).

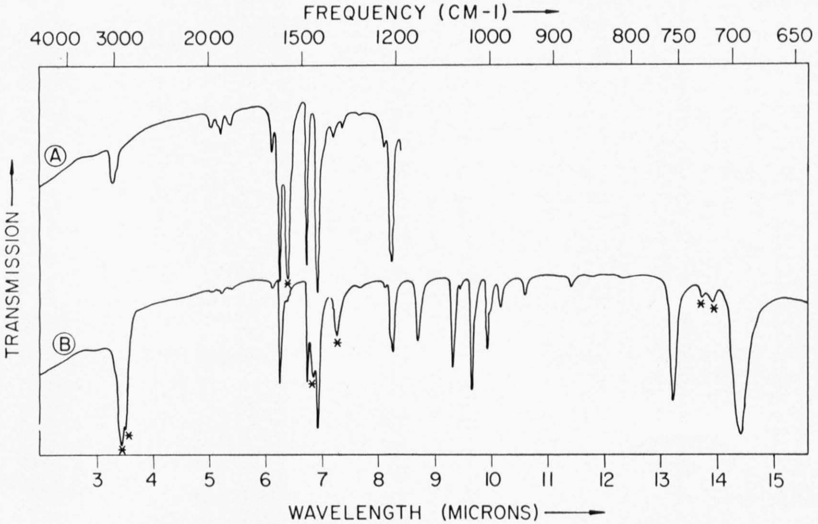

Fig. 3. The infra-red spectrum of $Co(Py)_4Cl_2$. A, B see Fig. 1. * Bands due to mulling-agent.

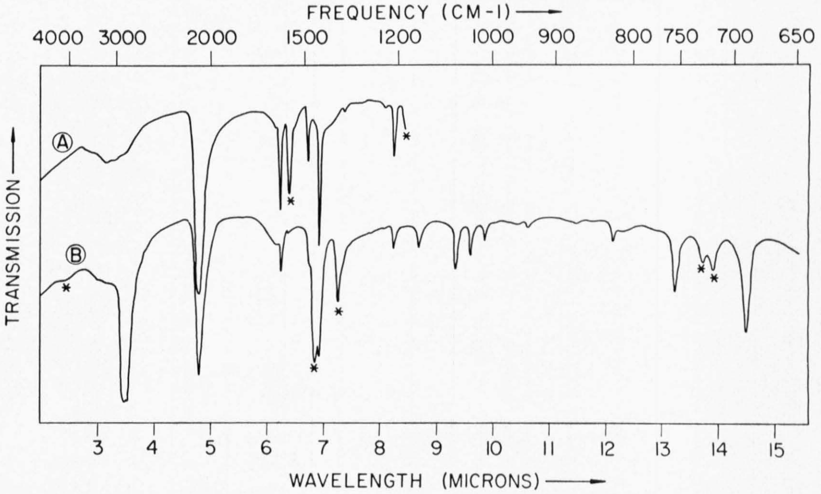

Fig. 4. The infra-red spectrum of $Cu(Py)_2(NCS)_2$. A, B see Fig. 1. * Bands due to mulling-agent (the bands at ca. 3.5 μ in B are due to vaseline).

Pyridine[15]		$Co(Py)_4(NCS)$	$Ni(Py)_4(NCS)_2$	$Co(Py)_4Cl_2$	$Cu(Py)_2(NCS)_2$
gas.	liq.				
—	650 w.	653 w.	—	—	—
679	675 w.	—	—	—	—
686	—				
699	—	700 vs. vsp.	699 vs. sp.	690 vs.	690 vs. sp.
706	702 vs.	—	—	—	—
716	—	712 vs. vsp.	711 vs. vsp.	—	—
743	749 s.	756 vs. vsp.	756 ms. sp.	757 vs. sp.	756 vs. sp.
759		767 vs. vsp.	767 s. sp.	—	—
815	810 w.	803 ms. sp.	800 ms. sp.	—	825 w. sp.
854	848 vw.	—	—	—	—
	885 w.	884 w. sp.	882 w.	876 w.	—
936	944 w.	950 w. sp.	—	943 w.	943 w.
983	991 s.	968 w. sp.	—	984 w.	—
999	—	996 w. sp.	—	1002	—
—	—	1006 ms. sp.	1005 s. sp.	1007 sh.	1014 ms. sp.
1023	1031 s.	1037 sh.	1036 ssp.	1035 vs. sp.	—
1039		1042 ms. sp.	1041 sh.	1057 w.	1042 s. sp.
1066	1069 s.	1070 ms. sp.	1067 s. sp.	1072 v. sv. sp.	1073 s. sp.
1081	1085 w.	—	—	—	—
1134					
1142	1146 s.	1147 w. sp.	1145 w.	1149 s. sp.	1149 ms. sp.
1152					
1207	1200 w.	1212 ms. sp.	1207 ssp.	1212 s. sp.	1212 ms. sp.
—	—	1214 sh.	1212 sh.	$\sim$1214 sh.	—
1226	1218 s.	1238 w. sh.	1230 w.	1232	1233 w. b.
1276	—	—	—	—	—
1290	1293 w.	1294 w. sp.	—	1304 w. b.	—
1353	1360 w.	1357 w. sp.	1355 w.	1355 w.	1353 w.
1368	1378 w.	—	—	1385 w.	—
1431	1439 s.	—	—	—	—
1443		1443 vs. sp.	1441 vs. sp.	1443 vs. vsp.	1443 vs. sp.
1467	—	—	—	—	—
1487	1485	1486 ms. sp.	1484 ms. sp.	1484 vs. vsp.	1484 m. sp.
1587	1584 vs.	1572 w. sp.	1565 w.	1567 w.	1570 w.
—	1600 s.	1603 s. sp.	1595 ms. sp.	1600 vs. vsp.	1603 s. sp.
1638	1636 w.	1631 w. sp.	1631 w. sp.	1631 ms. sp.	—
—	—	2070 vvs. sp.	2079 vvs. vsp.	—	2083 vs.
—		3049 vw. sp.	3058 w.	3030 w.	—

vs.=very strong; s.=strong; w.=weak; vw.=very weak; vvw.=very very weak; sp.=sharp; sh.=shoulder; ms.=medium strong.

Table 1. The frequencies of the infra-red bands of pyridine, $Co(Py)_4(NCS)_2$, $Ni(Py)_4(NCS)_2$, $CoCl_2(Py)_4$ and $Cu(Py)_2(NCS)_2$. (All frequencies are given in cm^{-1}.)

meter. Standard techniques for solid materials, viz. KBr-pellets, vaseline and hexachlorobutadiene mulls were used.

Results and Discussion

The vibrational frequencies of the compounds are given in Table 1 and their spectra are shown in Figs. 1 – 4.

The Pyridine Bands

The infra-red spectrum of the pyridine in the complexes is virtually identical with that of pyridine (liq.) [15, 16], except that some of the weaker bands do not appear. The bands appear, however, at slightly higher frequencies than in the gas [15]. The pyridine bands of the complexes are very narrow, and in most cases, very sharp (see Figs. 1 – 4).

The NCS^- Bands

To obtain the NCS^- bands, the spectra of the chloride salts [e. g. $Co(Py)_4Cl_2$; see Fig. 3] were subtracted from those of the thiocyanate [e. g. $Co(Py)_4(NCS)_2$] salts. The frequencies of the vi-

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[15] D. A. Long et al., Trans. Faraday Soc. **53**, 1171 [1957].

[16] J. K. Wilmshurst and H. J. Bernstein, Canad. J. Chem. **35**, 1183 [1957].

brations of the NCS^- ion in the compounds studied, are given in Table 2.

	$Co(Py)_4(NCS)_2$	$Ni(Py)_4(NCS)_2$	$Cu(Py)_2(NCS)_2$
	(light red)	(light blue)	(green)
ν_1	2070 cm^{-1}	2079 $\mathrm{cm}^{-\varepsilon}$	2083 cm^{-1}
ν_3	767	767	825
	(712)	(711)	—
$2\,\nu_2$	968	—	—

Table 2. The vibrational frequencies of the NCS group in $Co(Py)_4(NCS)_2$, $Ni(Py)_4(NCS)_2$ and $Cu(Py)_2(NCS)_2$.

The high "background" absorption in most of the samples in the $2-4\ \mu$ region is mainly due to the strong absorption peaks in the visible and near infra-red regions of these pyridine salts. There is also some (unresolvable) fine structure on the low-frequency wing of ν_1 which causes the asymmetry and apparent broadening of the band at its base.

(a) *$Co(Py)_4(NCS)_2$ and $Ni(Py)_4(NCS)_2$*

A preliminary X-ray investigation by PORAI–KOSHITS[17] of these compounds shows that the crystal is built up of separate $Me(Py)_4(NCS)_2$ units, with the NCS-ions in the *trans* position. The SCN – Me – NCS groups are linear and are bonded to Me through the N atom. The structure is thus *trans* di-isothiocyanate-tetrapyridine Me(II). The compounds are isomorphous, belonging to the monoclinic system (space group C2/c or Cc) with four molecules per unit cell.

The $N-C_S$ stretching vibration in $Co(Py)_4(NCS)_2$ and $Ni(Py)_4(NCS)_2$ occur at 2070 and 2079 cm^{-1} respectively (see Figs. 1 and 2). PORAI–KOSHITS gives a $N-C_S$ distance of 1.07 ± 0.06 Å. If this is correct, the $N-C_S$ stretching vibration should occur at a frequency of ca. 2300 cm^{-1} (the N – C distance in organic nitriles is 1.15 Å, $\nu_{C-S} \sim 2250\ \mathrm{cm}^{-1}$). The C – N frequency of 2070 cm^{-1} implies (empirically, from a graph of d_{C-N} vs. frequency) a d_{C-N} of 1.20 – 1.21 Å, i. e. a distance close to that of the $N=C$ bond. This throws some doubt upon the PORAI–KOSHITS' N – C bond-length in these compounds. The $N-C_S$ bond-length determined spectroscopically shows that the bond is intermediate between $N\equiv C$ and $N=C$ (PORAI–KOSHITS considers it as a pure $N\equiv C$ bond). The structure probably involves resonance between the canonical structures $Me-N\equiv C-S$ and $Me=N=C=S$.

PORAI–KOSHITS reports that the magnetic moments of the Co- and Ni-complexes are 4.84 and 3.01 B.M. respectively, and states that the NCS-group enters the inner complexing sphere of the metal ion, i. e. that $(n-1)\,d^2nsp^3$ hybrids are formed. This is in conflict with the magnetic data. nsp^3d^2 hybridization („Normalkomplex") would lead to two unpaired electrons (2.83 B.M.; spin only) for the Ni-compound and three for the Co-compound (3.87 B.M.; spin only). This is in accordance with the magnetic data; there is a large orbital contribution in the Co-complex.

The other bands in the infra-red spectrum of $Co(Py)_4(NCS)_2$ and $Ni(Py)_4(NCS)_2$ (Figs. 1 and 2) can readily be assigned to the pyridine vibrations (Table 1), except the four bands at 700, 712, 756 and 767 cm^{-1}. There are two strong bands in Py(liq) in this region viz., 702 and at 749 cm^{-1}. The two strong bands of the complex at 700 and 756 cm^{-1} can thus be assigned to the 700 and 749 cm^{-1} vibrations of pyridine.

There are various possible assignments of the two remaining bands:

1. The S – C vibration seems to be doubled, as in the case of $[Co(III)(en)_2Cl(NCS)]\,(NCS)$, where two different kinds of NCS-groups are present[8]. This is in conflict with the crystal structure[17].

2. Another possibility is that the SCN – Co – NCS chain is not perfectly linear. This would cause the symmetric S – C vibration to become active (see above). 50 cm^{-1} seems to be too large for this kind of splitting. In addition, there is no indication of splitting in the N – C stretching vibration.

3. Pyridine gas[16] has the following bands in this region: 686(52), 699(70), 706(64), 716(58), 743(32) and 759(4) cm^{-1} (numbers in brackets give the % abs. at 0.24 mm). In Py(liq) the spectrometer traces a composite envelope for the first three bands at 702 cm^{-1}, and the 743 cm^{-1} band appears at 749 cm^{-1} in the liquid. The 711 cm^{-1} band of the complex can thus be assigned to the pyridine band which occurs at 716 cm^{-1} in the gas. The 767 cm^{-1} band is thus due to the S – C stretching vibration of the SCN group. This assignment confirms the fact that the SCN group in these complexes cannot be described by $Me-N=C-S$, but as resonating between the two canonical structures

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[17] M. A. PORAI-KOSHITS and A. S. ANTSYSHKINA, Kristallografiya **3**, 686 [1960].

(above). The value of d_{C-S} (1.74) given by Porai–Koshits seems too high.

(b) *α-Co(Py)$_2$(NCS)$_2$ and Cu(Py)$_2$(NCS)$_2$*

It was found that when $Co(Py)_4(NCS)_2$ is heated for one hour, it loses 2 Py molecules, forming $Co(Py)_2(NCS)_2$ (probably the α-isomer). The crystal structure[18] is monoclinic [isomorphous with $Cu(Py)_2(NCS)_2$], space group C2/m with 2 molecules per unit cell. The Co is SIX co-ordinated through both N and S of the NCS, forming chains of octahedra along the *c*-axis.

ν_{N-C} occurs at 2101 cm^{-1} (vs. sp). The 712 cm^{-1} pyridine band has disappeared, the rest of the pyridine bands remain the same. The 767 cm^{-1} NCS band disappeared and is replaced by a weak, broad band at ca. 780 cm^{-1}, which can be assigned to the ν_{C-S} vibration. The simple relation between d_{C-N} and ν_{C-N} (or d_{C-S} and ν_{C-S}) would probably be altered by the co-ordination of the NCS group through both the N and the S atoms. Two effects would probably play an important role, viz. (i) the resonance-effect discussed above, which causes a lowering in the $C \equiv N$ triple-bond character (decrease in ν_{C-N}) and an increase in the $C-S$ double bond character (increase in ν_{C-S}), and (ii) the effect of the double co-ordination. If only (i) occurs, then ν_{CN} should be lowered while ν_{CS} is raised in frequency. In the compounds where SCN^- is co-ordinated through both N and S, *both* frequencies are raised as compared to the pure $N=C$ double bond and the pure $S-C$ single bond*. In these compounds it seems that the $N-C$ bond has more triple-bond character and the $C-S$ bond has more double-bond character than in the $Me(Py)_4(NCS)_2$ compounds, where the co-ordination is only through nitrogen.

The same applies to the case of $Cu(Py)_2(NCS)_2$, which is isomorphous with $Co(Py)_2(NCS)_2$[18] (see Fig. 4).

Conclusions

The pyridine bands in the pyridine complexes of Co, Cu and Ni are very sharp and can be directly correlated with the bands of Py(g). From the position of the NC stretching vibration in $Co(Py)_4(NCS)_2$ it is concluded that the Porai–Koshits'[17] bond length is probably wrong.

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[18] M. A. Porai-Koshits and G. N. Tischenko, Kristallografiya **4**, 239 [1960].

* $K_2Hg(SCN)_4$: $\nu_{CN}=2100$ cm^{-1}, $\nu_{CS}=716$ cm^{-1} (co-ordinated through S); $CoHg(SCN)_4$: $\nu_{CN}=2142$ cm^{-1}, $\nu_{CS}=793$ cm^{-1} (co-ordinated through both N and S; infra-red data, see refs. [8, 12]). KCNS: $\nu_{CN}=2066$ cm^{-1}, $\nu_{CS}=748$ cm^{-1}. These values clearly reflect the partial double bond character of both $N \equiv C$ and $C-S$ in KNCS.