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Short communication

STRUCTURAL INFORMATION ON THE COORDINATION COMPOUNDS FORMED BY MANGANESE(II), COBALT(II), NICKEL(II), ZINC(II), CADMIUM(II) AND MERCURY(II) THIOCYANATES WITH 2-, 3- AND 4-BENZOYLPYRIDINES FROM THEIR MAGNETIC MOMENTS, ELECTRONIC AND INFRARED SPECTRA

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The donor properties of pyridine and its ring substituted derivatives have been the subject of several investigations. However, coordination compounds of benzoylpyridines, i.e. pyridine derivatives with a —COC_6H_5 group in 2-, 3- and 4- positions in the ring, have received little attention. Benzoylpyridines possess two potential donor sites: (i) pyridine ring nitrogen, and (ii) the carbonyl oxygen in the side chain, which raises the possibility of linkage isomerism. With monodentate ligands bonding may occur through any one of these sites. One cannot rule out the possibility of the two coordination sites bonding to different metal ions (bidentate bridging ligand) resulting in polymeric structures. It should be possible to distinguish between the likely modes of metal—benzoylpyridine bonding using IR spectroscopy. Although some complexes of 2-benzoylpyridine with metal(II) salts are known [1—3] the donor ability of 3- and 4-benzoylpyridines has, however, not attracted much attention and only a few complexes of metal(II) halides with these ligands have been reported [4, 5]. The replacement of halides by potentially multidentate thiocyanate groups offer interesting bonding possibilities. The present study on the preparation, magnetic susceptibilities, electronic and IR spectral features down to 200 cm^{-1} on the coordination compounds formed by the interaction of maganese(II), cobalt(II), nickel(II), zinc(II), cadmium(II) and mercury(II) thiocyanate with 2-, 3- and 4-benzoylpyridines has been undertaken to elucidate the mode of metal—benzoylpyridine and of metal—thiocyanate bondings. It is shown that 3- and 4-benzoylpyridines, though potentially bidentate ligands, act only as terminally bonded monodentate ligands, bonding through their pyridine ring nitrogen atoms only. 2-Benzoylpyridine, on the other hand, is shown to act as monodentate ligand bonding through its pyridine ring nitrogen and also as a bidentate chelating

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ligand bonding through the carbonyl oxygen as well. Tentative stereochemistries of the compounds isolated in the solid state have been proposed. Further, the ligand field parameters 10 Dq, B and β calculated for the manganese(II), cobalt(II) and nickel(II) complexes are consistent with their proposed stereochemistries.

EXPERIMENTAL

2-, 3- and 4-Benzoylpyridines were obtained from M/s. Ega Chemicals, West Germany, and used as such. The manganese(II), cobalt(II), nickel(II), zinc(II) and cadmium(II) thiocyanate complexes were synthesized by adding an excess of the benzoylpyridine to a hot ethanolic solution of the respective metal(II) thiocyanate. The products which precipitated immediately or crystallized out on cooling were suction-filtered, washed with ethanol and dried in an air oven at 70° C. The compounds $Co(3\text{-}BOP)_4(NCS)_2$, $Co(4\text{-}BOP)_4(NCS)_2$ and $Ni(4\text{-}BOP)_2(NCS)_2$ were obtained by heating their diethanolates at ca. 120° C in an air oven. The mercury(II) thiocyanate complex was obtained by boiling a suspension of the metal(II) thiocyanate in ethanol with an excess of the respective benzoylpyridine and the mixtures were filtered hot. The complexes which crystallized out on cooling were suction-filtered, washed with ethanol and dried. Stoichiometries of the solid complexes isolated were established by gravimetric metal and thiocyanate estimations.

Electronic spectra of the manganese, cobalt and nickel complexes were recorded as nujol mulls in the range 33000—6000 cm^{-1} on a Cary 14 recording spectrophotometer. The mulls were smeared on filter paper and run against a reference consisting of a similar piece of filter paper soaked in nujol. Infrared spectra of the uncoordinated benzoylpyridines and of their thiocyanate complexes studied were recorded as nujol mulls on a Perkin—Elmer 621 spectrophotometer equipped with caesium iodide optics. The mulls were supported between sodium chloride plates (rock salt region) and thin polythene sheets (650—200 cm^{-1}). Magnetic susceptibilities were measured at room temperature by Faraday's method with a Cahn R.G. Electrobalance Model 7550 using $HgCo(NCS)_4$ as the magnetic susceptibility standard. Pascal's constants were used for diamagnetic corrections and the magnetic moments were calculated using the equation

$$\mu_{\text{eff}} = 2.84\ (x_{\text{M}}^{\text{corr}}T)^{1/2}$$

RESULTS AND DISCUSSION

The complexes isolated in the present study, their analytical data, characteristics IR bands in the uncoordinated benzoylpyridines and in their complexes with metal(II) thiocyanates studied here are listed in Table 1. Their room temperature magnetic moments, observed bands in the electronic spectra and the ligand field parameters are recorded in Table 2.

TABLE 1

Analytical data for benzoylpyridine and thiocyanate modes (cm^{-1})

Compound	Metal (%)	Thio-cyanate (%)	νC—O	Ring vibrations	νCN	νCS	δNCS	νM—NCS or νM—SCN
2-BOP			1654	990, 603, 401				
3-BOP			1657	999, 601, 402				
4-BOP			1655	998, 601, 405				
Mn(2-BOP)$_2$(NCS)$_2$	10.31 (10.24)	21.80 (21.60)	1615	1015, 622, 445	2070	813	470 455	300
Mn(3-BOP)$_4$(NCS)$_2$	6.12 (6.09)	12.90 (12.84)	1654	1040, 625, 415	2075	814	471 450	300
Mn(4-BOP)$_4$(NCS)$_2$	6.13 (6.09)	13.10 (12.84)	1654	1025, 630, 423	2065	816	482 472	302
Co(2-BOP)$_2$(NCS)$_2$	11.10 (10.91)	21.51 (21.44)	1615	1008, 630, 421	2090	818	470 450	270
Co(3-BOP)$_4$(NCS)$_2$	6.57 (6.51)	12.90 (12.79)	1655	1027, 635, 440	2075 2060	819	488 478	285
Co(3-BOP)$_4$(NCS)$_2$(EtOH)$_2$	6.00 (5.91)	11.70 (11.61)	1655	1025, 632, 435	2067 2050	838	484 473	292
Co(4-BOP)$_4$(NCS)$_2$(EtOH)$_2$	6.12 (5.91)	11.80 (11.61)	1655	1020, 637, 434	2067	835	485 475	300
Co(4-BOP)$_4$(NCS)$_2$	6.60 (6.51)	12.63 (12.79)	1652	1024, 632, 430	2065 2050	814	482 472	300
Ni(2-BOP)$_2$(NCS)$_2$	11.10 (10.91)	21.55 (21.44)	1605	1008, 630, 423	2100 2060	815	465	295
Ni(3-BOP)$_4$(NCS)$_2$	6.59 (6.51)	12.91 (12.79)	1656	1025, 632, 435	2065	838	485 475	275
Ni(4-BOP)$_2$(NCS)$_2$(EtOH)$_2$	9.50 (9.32)	18.50 (18.32)	1650	1013, 635, 430	2070	825	482 473	285
Ni(4-BOP)$_2$(NCS)$_2$	11.10 (10.91)	21.60 (21.44)	1650	1010, 637, 435	2110	830	470 460	260
Zn(2-BOP)$_2$(NCS)$_2$	12.00 (11.88)	21.40 (21.21)	1650	1016, 640, 420	2100	813	475	300
Zn(3-BOP)$_2$(NCS)$_2$	11.78 (11.88)	21.33 (21.21)	1653	1022, 640, 430	2070 2050	815	470	300
Zn(4-BOP)$_2$(NCS)$_2$	12.10 (11.88)	21.40 (21.21)	1653	1020, 640, 440	2080	828	475 470	305
Cd(2-BOP)(NCS)$_2$	27.50 (27.25)	28.40 (28.22)	1620	1004, 628, 415	2100	680	460 450	270
Cd(3-BOP)$_2$(NCS)$_2$	19.10 (18.85)	19.65 (19.53)	1650	1024, 645, 426	2100	760	460 450	
Cd(4-BOP)$_2$(NCS)$_2$	1900 (18.85)	19.50 (19.53)	1650	1020, 620, 430	2090	760	470 460	
Hg(3-BOP)(SCN)$_2$	4020. (40.10)	23.50 (23.30)	1658	1027, 630, 425	2136	695	443 429	297
Hg(4-BOP)(SCN)$_2$	40.20 (40.10)	23.5 (23.30)	1652	1020, 618, 425	2138	700	450 432	300

Benzoylpyridines possess two potential donor sites: (i) pyridine ring nitrogen, and (ii) oxygen of the carbonyl group. Significant IR absorption bands due to the carbonyl group is the νCO which absorbs at ca. 1650 cm^{-1} in the uncoordinated benzoylpyridines. The carbonyl stretching frequency is known to suffer significant negative shift (40—60 cm^{-1}) in metal complexes with amides and other carbonyl donors because of coordination through carbonyl oxygen [6]. On the other hand, coordination through the pyridine ring nitrogen results in significant perturbations in the fundamental frequencies

TABLE 2

Magnetic moments (B.M.), electronic spectral bands and ligand field parameters (cm^{-1})

Compound	μ_{eff}	ν_1	ν_2	ν_3	10 Dq	B	β
Mn(2-BOP)$_2$(NCS)$_2$	6.11	21770	22600	26320	9228	921	0.96
Mn(3-BOP)$_4$(NCS)$_2$	6.00	16660		26630	9838	911	0.93
Mn(4-BOP)$_4$(NCS)$_2$	5.98	19230	21740	26310	8864	777	0.81
Co(2-BOP)$_2$(NCS)$_2$	4.87	9090	18350	23810	9260	926	0.95
Co(3-BOP)$_4$(NCS)$_2$(EtOH)$_2$	4.77	9663	16130	20200	6467	490	0.50
Co(3-BOP)$_4$(NCS)$_2$	5.07	9500		21050	9517	771	0.79
Co(4-BOP)$_4$(NCS)$_2$(EtOH)$_2$	4.99	8307	15880	21270	7573	815	0.84
Co(4-BOP)$_4$(NCS)$_2$	5.02	9500	16340	26670	6839	967	0.99
Ni(2-BOP)$_2$(NCS)$_2$	3.32	8757	16630	22420	9757	652	0.63
Ni(3-BOP)$_4$(NCS)$_2$	2.97	10530	17090		10530	932	0.89
Ni(4-BOP)$_2$(NCS)$_2$(EtOH)$_2$	3.87	8333	16400	21050	8333	830	0.79
Ni(4-BOP)$_2$(NCS)$_2$	3.29	8474	16500	21330	8474	827	0.79

of the pyridine part of the molecule. The pyridine ring vibrations at ca. 990, 600 and 400 cm^{-1} in uncoordinated benzoylpyridines undergo significant positive shifts upon coordination through pyridine ring nitrogen. Benzoylpyridines may also coordinate through both their bonding sites and may act as bidentate bridging or chelating ligands.

The CO stretching vibration of the uncoordinated 3- and 4-benzoylpyridines remains either unperturbed or undergoes slight positive shift in the metal(II) thiocyanate complexes studied here (Table 1). This clearly indicates that the carbonyl group is inert towards coordination in all the metal(II) thiocyanate complexes with both these ligands. On the other hand, IR spectra of the complexes under investigation exhibit appreciable perturbations in the fundamental frequencies of the pyridine part of the molecule and indicate conclusively that coordination of 3- and 4-benzoylpyridines investigated here takes place via their pyridine ring nitrogen atoms only [7, 8].

In the case of 2-benzoylpyridine complexes in addition to the significant positive shifts of the pyridine ring vibrations, the CO stretching vibration suffers a significant shift (except in the case of zinc(II) thiocyanate complex) and occurs at ca. 1620 cm^{-1} indicating thereby that this ligand is acting as a bidentate chelating ligand in the metal(II) thiocyanate-2-benzoylpyridine complexes studied here.

Manganese(II), cobalt(II) and nickel(II) complexes

The room temperature magnetic moment values, electronic spectral bands and ligand field parameters of all the manganese(II), cobalt(II) and nickel(II) thiocyanate complexes with the ligands investigated suggest octahedral stereochemistry around the metal(II) ions [9—11]. IR spectra indicate a significant positive shift of the pyridine ring vibrations (Table 1) consistent with coordination through pyridine ring nitrogen by all the benzoylpyridines. In addition to coordination through the pyridine ring nitrogen atom the 2-benzoylpyridine is also coordinated through the carbonyl group (bidentate ligand) as is evident from the negative shift of the νCO band in the manganese(II), cobalt(II) and nickel(II) thiocyanate complexes with 2-benzoylpyridine. IR bands due to thiocyanate groups (Table 1) suggest the exclusive presence of terminally N-bonded NCS groups in all these complexes except in the 1:2 nickel(II) thiocyanate—4-benzoylpyridine complex in which their frequencies are consistent with bridging NCS groups [12]. Moreover, IR spectra indicate that the ethanol molecules are coordinated only in $Ni(4\text{-}BOP)_2(NCS)_2(EtOH)_2$ complex. Based on the considerations of room temperature magnetic moment values, electronic spectral bands, ligand field parameters and the IR bands due to coordinated benzoylpyridines and the NCS groups the tentative stereochemistries of the above complexes are postulated as: (i) six-coordinate monomeric structures with an octahedral environment of two oxygen atoms (from two benzoylpyridine molecules) and four nitrogen atoms (two from 2-benzoylpyridine molecules and two from terminally N-bonded NCS groups) around the metal(II) ions in the solid state for $Mn(2\text{-}BOP)_2(NCS)_2$, $Co(2\text{-}BOP)_2(NCS)_2$ and $Ni(2\text{-}BOP)_2(NCS)_2$ complexes; (ii) $Mn(3\text{-}BOP)_4(NCS)_2$, $Mn(4\text{-}BOP)_4(NCS)_2$, $Co(3\text{-}BOP)_4(NCS)_2(EtOH)_2$, $Co(3\text{-}BOP)_4(NCS)_2$, $Co(4\text{-}BOP)_4(NCS)_2(EtOH)_2$, $Co(4\text{-}BOP)_4(NCS)_2$ and $Ni(3\text{-}BIO)_4(NCS)_2$ complexes as monomeric, six-coordinated structures with an octahedral environment of six nitrogen atoms (four from four pyridine ring nitrogen bonded benzoylpyridine molecules and two from terminally N-bonded NCS groups) around the metal(II) ions (with non-coordinated ethanol molecules in the ethanolate complexes) in the solid state; (iii) a six-coordinate monomeric structure with an octahedral environment of two oxygen atoms (from coordinated ethanol molecules) and four nitrogen atoms (two from pyridine ring nitrogen bonded benzoylpyridine molecules and two from terminally N-bonded NCS groups) around the nickel(II) ions in the $Ni(4\text{-}BOP)_2(NCS)_2(EtOH)_2$ complex; and (iv) a six-coordinate polymeric octahedral structure with the adjacent metal ions linked by two —SCN— bridges to form quasi-planar eight-membered rings —$Ni(NCS)_2Ni$— for the $Ni(4\text{-}BOP)_2(NCS)_2$ complex in the solid state.

Zinc(II), cadmium(II) and mercury(II) complexes

The magnetic susceptibility and ligand field measurements though yielding useful structural information on transition metal complexes are not, however, applicable to d^{10} systems (divalent zinc, cadmium and mercury compounds) as these have closed shells of valence electrons. Information on the tentative stereochemistries of their compounds in the present study has been derived from a comparison of metal—benzoylpyridine and metal—thiocynate bondings with similar modes in complexes whose structures have been established by X-ray crystallography and/or magnetic susceptibility, electronic and IR spectral studies.

Zinc(II) complexes

Zinc(II) thiocyanate gave 1:2 complexes with all the benzoylpyridine investigated. In addition to the ligand bands indicating the exclusive presence of pyridine ring nitrogen bonded 2-, 3- and 4-benzoylpyridine molecules, IR spectra of these complexes show absorption bands at ca. 2080, 820, 470, 450 and 300 cm^{-1}. These new bands are identified (Table 1) as due to coordinated thiocyanate groups and their frequencies are consistent with the exclusive presence of terminally N-bonded NCS groups [12]. It is therefore suggested that the metal atoms in all these complexes have four-coordinate monomeric tetrahedral environments of four nitrogen atoms (two from two pyridine ring nitrogen bonded benzoylpyridine molecules and two from terminally N-bonded NCS groups) in the solid state. The observed frequencies due to coordinated thiocyanate groups rule out the possibility of thiocyanate-bridged polymeric octahedral structures for these complexes.

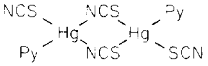
Cadmium(II) complexes

Cadmium(II) thiocyanate gave a 1:1 complex with 2-benzoylpyridine but 1:2 with 3- and 4-benzoylpyridines. IR bands clearly indicate the presence of bidentate chelating 2-benzoylpyridine in the 1:1 cadmium(II) thiocyanate—2-benzoylpyridine complex. Moreover, IR bands at 2100, 680, 460, 450 and 270 cm^{-1} indicate the exclusive presence of terminally S-bonded NCS groups in this complex [12]. Based on these considerations the 1:1 cadmium(II) thiocyanate-2-benzoylpyridine complex is tentatively assigned a monomeric four-coordinate structure with a tetrahedral environment of one oxygen and one nitrogen atom (both from bidentate chelating 2-benzoylpyridine molecule) and two sulphur atoms (from two S-bonded SCN groups) around cadmium(II) in the solid state.

The 1:2 cadmium(II) thiocyanate complexes with 3- and 4-benzoylpyridines may be postulated to have either (i) four-coordinated monomeric tetrahedral structures with terminal N- or S-bonded NCS groups, or (ii) six-coordinate, thiocyanate-bridged polymeric octahedral structures. The observed frequencies of νCN, νCS and δNCS modes in both these complexes (Table 1) are in agreement with similar modes in $ML_2(NCS)_2$ complexes (M = Mn(II), Fe(II), Co(II), Ni(II) and L = a monodentate ligand) shown by X-ray crystallography and/or magnetic and IR spectral measurements to have bridging thiocyanate groups [12]. Both these complexes may thus be assigned six-coordinate polymeric octahedral structures with the adjacent metal atoms linked by two —SCN— bridges to form quasi-planar eight membered rings —$Cd(SCN)_2Cd$—.

Mercury(II) complexes

Mercury(II) thiocyanate gave 1:1 complexes with 3- and 4-benzoylpyridines but did not react with 2-benzoylpyridine under similar conditions. IR spectra indicate the exclusive presence of terminally pyridine ring nitrogen bonded 3- and 4-benzoylpyridines in these complexes. The observed frequencies due to coordinated thiocyanate groups in both these complexes (Table 1) are consistent with terminally S-bonded thiocyanate groups [12]. Both these complexes are thus tentatively assigned to have monomeric three-coordinated structures in the solid state. Thiocyanate-bridged dimeric structures with both terminal and bridging thiocyanate groups



(Py = 3- or 4- benzoylpyridine)

or six-coordinated polymeric octahedral structures with only bridging thiocyanate groups for these 1:1 complexes ruled out as the fundamental vibrations due to coordinated thiocyanate groups indicating the exclusive presence of terminally S-bonded SCN groups in both these complexes. It may be pointed out that the frequency of νHg—S of $Hg(SCN)_2$ [13] suffers only a small negative shift in the mercury(II) thiocyanate complexes studied here (Table 1). This may be attributed to the fact that there are two sets of antibonding π-orbitals localized on the sulphur atom which along with the vacant *d*-orbitals of the sulphur atom can accept electron density from the filled non-bonding *d*-orbitals of the mercury atoms thus resulting in strengthening of the Hg—S bond. In spite of the higher mass of mercury than cadmium the frequency of νM—SCN in the mercury(II) thiocyanate complexes occurs at higher energies compared with cadmium(II) thiocyanate complexes. This is probably because of the greater covalent character of the Hg—SCN bond relative to the Cd—SCN bond. The effect of mass on the νM—SCN in the complexes of cadmium(II) and mercury(II) appears to be compensated by the reverse effect of the covalent charactre of the metal—ligand bond. The assignment of νM—NCS and νM—SCN modes in the present study (305–260 cm^{-1}) must be considered as tentative since the internal modes of the ligands used are also expected to occur in this region. These bands could also be assigned to a ligand mode which had become lowered in frequencies or become IR spectra on cooridnation to a heavy metal atom. The tentative stereochemistries and the isomorphous nature of the metal(II) thiocyanate complexes studied herein has been derived from a comparison of their magnetic moments, electronic spectral data, ligand field parameters and of their coordinated anionic modes with those of compounds of established structures. However, unambiguous characterization of these compounds should be based on complete crystal structure determination.

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