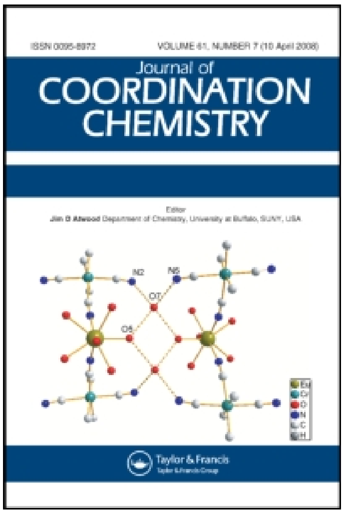

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Sudhir Burman[ab]; D. N. Sathyanarayana[a]
[a] Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India [b] Chemistry Department, Drexel University, Philadelphia, PA

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IRON(II, III) COMPLEXES WITH *N,N′*-DI(2-)PYRIDYL THIOUREA. MÖSSBAUER AND OTHER SPECTROSCOPIC STUDIES

SUDHIR BURMAN† and D. N. SATHYANARAYANA

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India

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Several iron(II, III) complexes of *N,N′*-di(2-)pyridyl thiourea have been synthesized. The preparation of the complexes from iron(III) salts proceeds through a reduction of iron(III) to iron(II) followed by a subsequent reoxidation. The Mössbauer, electronic and infrared spectra of these complexes have been measured. The results are concordant with the coordination of pyridine nitrogens and thiocarbonyl sulfur yielding polymeric complexes. A variable temperature NMR study of the free ligand shows that two conformation are accessible for it in solution at subambient temperatures.

INTRODUCTION

Currently the study of conformational properties and chelating ability of bridged molecules containing pyridine (Py), of the type Py-X-Py (where X = S, SO_2 CO, etc.) is of special interest.[1–4] It was established that these ligands normally behave as bidentates and that the knowledge of the ligand molecular conformation is useful for the prediction of the stereochemistry of the metal complexes. An investigation in this context of the synthesis and characterization of the complexes of *Sym. N,N′*-di(2-)pyridyl thiourea (PyNHCSNHPy) (DPyTU) with iron (II, III) salts is described here. Save for a preliminary report by Banerjea and Singh,[5] the donor characteristics of DPyTU has not been investigated. Further interest in DPyTU is the identification of minimum energy conformations[6] and as prospectives for antiviral chemotherapy.[7] Variable temperature proton NMR spectroscopy was presently employed to determine the more stable conformers. Even though thiourea derivatives coordinate only through sulfur,[8,9] interesting possibilities are however introduced when the substituent has a site of coordination. For instance, *N*-phenyl *N′*-pyridyl thiourea is reported[10] to display three different types of coordination behavior depending upon the nature of the metal ion, the anion and the substituent on the phenyl ring.

EXPERIMENTAL

Materials

All the commercially available chemicals used were of analytical grades. *Sym. N,N′*-di(2-)pyridyl thiourea was prepared and purified by the procedure of Fischer.[11] M.P. 153–154°; Literature 155°C.

Physical Measurements

The infrared spectra (4000–400 cm^{-1}) were recorded as KBr discs and Nujol mulls with a Carl Zeiss UR 10 spectrophotometer. The electronic absorption spectra (180–1400 nm) were obtained with a Unicam SP 700 A spectrophotometer; the spectra were recorded in methanol in the ultraviolet region and as solids by the KCl pellet technique in the visible region. The magnetic measurements were done using the Gouy method and $Hg[Co(CNS)_4]$ as a calibrant. The Mössbauer spectra of polycrystalline samples were measured at 293 K on a ECIL MBS 35 spectrometer in constant acceleration mode. ^{57}Co in Pd matrix was used as the source. The velocity scale was calibrated using the inner four lines of iron foil spectrum. The isomer shifts were measured relative to the centroid of sodium nitroprusside as zero velocity. The spectral data were fitted using a least squares program assuming lorentzian line shapes, the best fit obtained by varying all the parameters.[12] ^1H NMR spectra of free DPyTU were recorded at 270 MHz with a Bruker WH spectrometer equipped with Fourier transform accessories.

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†Present address: Chemistry Department, Drexel University, Philadelphia, PA 19104. To whom correspondence should be addressed.

Measurements were made with a variable temperature probe from 50 to −50°C. Chemical shifts are referred to internal TMS for solutions of ligand in $CDCl_3$.

Analysis Carbon and hydrogen were determined microanalytically; metal and anions were estimated by standard methods.

Preparation and Properties of the Complexes

Iron(III) halide and nitrate complexes were obtained by adding to a warm absolute ethanol solution of the metal salt (1 mmole), dehydrated with a few ml of 2,2-dimethoxypropane, a warm ethanol solution of the ligand (3 mmole) dropwise with stirring. A slow stream of oxygen was simultaneously bubbled through the reaction mixture. The solution was kept aside for ½ h and the brick red solid that separates out was washed with ethanol and ether and dried in vacuo. Similar procedure was utilized to prepare the halide and thiocyanate complexes of iron(II). Bubbling oxygen through the reaction mixture is not required, however.

To obtain iron(III) thiocyanate complex, an excess (10 mmole) of ammonium thiocyanate was added to an absolute ethanol solution of ferric chloride (1 mmole) and warmed to 50°C. A warm ethanol solution of the ligand (3 mmole) was added, dropwise with stirring, when simultaneously a slow stream of oxygen was bubbled through the reaction mixture. A deep red coloured complex separates out; it was collected, washed and dried as before.

The complexes are stable in air and insoluble in most of the common organic solvents. The analytical results are shown in Table I. Efforts to synthesize the complexes of DPyTU with iron(II, III) sulfates and iron(II) iodide did not yield compounds of definite stoichiometry.

RESULTS AND DISCUSSION

Under normal conditions, the reaction of DPyTU with iron(III) salts produces complexes which contain iron in ferrous state. This was established by magnetic susceptibility and Mössbauer studies. Therefore the synthesis of complexes of iron(III) salts with DPyTU proceeds via reduction to iron(II) with subsequent reoxidation to iron(III) by oxygen. The oxidation of thioureas by iron(III) salts is common, since a lower oxidation state is easily accessible.[13,14]

Infrared Spectra

Selected infrared frequencies of DPyTU and its complexes are shown in Table II. A region of interest lies between 1650 and 1450 cm^{-1}; the spectrum of DPyTU exhibits an intense band at 1605 cm^{-1} arising from C=N stretching coupled with C=C stretching mode of the pyridine ring. This band is shifted higher, 1620–1650 cm^{-1} in the complexes. A medium band at 1000 cm^{-1} corresponding to aromatic ring breathing mode is found in the complexes as a split band in the region 1010–1025 cm^{-1}. Further, another band, also of medium intensity, at 615 cm^{-1} of the free ligand attributable to out-of-plane ring deformation moves to 640 cm^{-1} in the metal complexes. These observations clearly demonstrate the coordination of DPyTU to iron through ring nitrogen.[15] The infrared spectra of the metal complexes do not display any absorptions corresponding to free pyridine and consequently suggest the bonding of both pyridine nitrogens of the ligand.

The strong absorptions at 1570 and 1530 cm^{-1} in the spectrum of free DPyTU originating from NCN stretching and in-plane N—H bending of thiourea skeleton are shifted by nearly 30 cm^{-1} to higher wave

TABLE I
Analytical data for DPyTU complexes.

		% Carbon		% Hydrogen		% Metal		% Anion	
Compound	Colour	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
Fe(DPyTU)Cl_3	brown	33.4	33.65	2.4	2.55	14.0	14.22	27.0	27.15
Fe(DPyTU)Cl_2	light brown	36.7	36.99	2.7	2.80	15.3	15.64	19.7	19.90
Fe(DPyTU)Br_3	deep brown	25.3	25.13	2.1	1.90	10.4	10.62	45.3	45.58
Fe(DPyTU)$Br_2 \cdot 2H_2O$	brown	26.9	27.43	3.1	2.90	11.4	11.59	33.0	33.15
Fe(DPyTU)$(NO_3)_3$	deep brown	27.8	27.98	2.0	2.12	11.6	11.82		
Fe(DPyTU)$(SCN)_3$	grey	36.4	36.54	2.3	2.17	12.0	12.14		
Fe(DPyTU)$(SCN)_2 \cdot 2H_2O$	brownish red	35.4	35.63	3.1	3.19	12.6	12.75		

TABLE II

Selected infrared frequencies (cm^{-1}) of DPyTU and its complexes.

Compound	νN—H		νC=C + νC=N (ring)	νC=N (amide)	δ N—H	δ C—H	Ring Breathing	νC=S	Ring def	δ C=S	¶ C=S
DPyTU = L	3255m	3180w	1605s	1570s	1540s	1105s	1000m	740m	615m	510m	415m
$FeCl_3 \cdot L$	3235mb	3170wb	1650s	1610s	1570s	1090w	1015wb	705m	640m	520w	420w
$FeCl_2 \cdot L$	3235mb	3190sh	1650s	1607s	1570s	1095w	1015wb	705m	640m	520m	420w
$FeBr_3 \cdot L$		3170wb	1620s	1600sh	1570s	1120w	1020m	720m 705m	630m	520m	420sh
$FeBr_2 \cdot L \cdot 2H_2O$		3180wb	1620s	1600m	1570m	1120w	1025m	720m	642m	520w	425w
$Fe(NO_3)_3 \cdot L$	3220wb		1620s	1600m	1570m	1125w	1020w	705m	632m	525m	425m
$Fe(SCN)_3 \cdot L$	3220vb		1605sb	1605sb	1560sb	1115w	1020m	730m	640m	535s	425m
$Fe(SCN)_2 \cdot L \cdot 2H_2O$		3180wb	1630s	1605s	1570sb	1115w	1020w	730s	638m	535m	425m

Abbreviations: ν = stretching, δ = in-plane bending, ¶ = out-of-plane bending.

numbers in the metal complexes suggesting sulfur coordination. In support of this, a medium band at 740 cm^{-1} in the free ligand attributable to C=S stretching[16] moves downwards by 20–30 cm^{-1} and the in-plane C=S bending mode assigned at 510 cm^{-1} increases by about 15 cm^{-1} in the spectra of metal complexes, thus clearly revealing the bonding of the metal ion via thione sulfur too.[16]

The complexes of iron(II, III) thiocyanates exhibit infrared absorptions, not present in the halide complexes, near 2090(s), 790(m), 475(m); and 2080(s), 785(m), 480(m) cm^{-1}, respectively corresponding to N-bonded thiocyanate.[17] Similarly, the infrared spectrum of the iron(III) nitrate complex displays new bands at 1485(s), 1340(w, br), 1030(m) and 830(w) cm^{-1}, attributable to a monodentately bonded nitrate group.[17]

Electronic Spectra

The Fe(II) complexes show electronic spectra in the 8000 to 11500 cm^{-1} region, which are slightly dependent on the nature of the anion in the complex. The intensity and width of the bands and the absence of these bands in Fe(III) complexes are taken as evidence that these bands correspond to *d*–*d* transitions. By using a curve resolver, the band positions were determined to be 11300 ± 200 cm^{-1} and 8500 ± 200 cm^{-1}. These two bands are the two components of the $^5E_g \leftarrow {}^5T_{2g}$ transition; the relatively large splitting seems to confirm the low symmetry around Fe(II) ion.[18] The 10*Dq* value thus found for DPyTU is about 10000 cm^{-1}. This value is somewhat larger compared to the 10*Dq* value of FeF_2 (8800 cm^{-1})[19] indicating a higher position for DPyTU in the spectrochemical series.

Magnetic Susceptibility and Mössbauer Spectra

The magnetic moment and Mössbauer spectral data are collected in Table III. The values of magnetic moments for iron(II) complexes establish that these are of high spin variety. The somewhat lower values arise from distortion from octahedral geometry[20,21] and also possibly due to antiferromagnetic interactions between iron atoms through the ligand. The values of the isomer shifts (*IS*) are rather lower than for most other high spin iron(II) compounds[21,22] for which the *IS* is on the average 1.4 mm/sec. This can be attributed to the considerable degree of covalency in the iron-sulfur bonds and to the distortion from octahdral symmetry. The values of quadrupole splitting (*QS*) are normal for six coordinated high spin iron(II).

TABLE III
Magnetic moments and Mössbauer parameters[a] of DPyTU complexes

Compound	Temp K	μ_{eff} B.M.	*IS*	*QS*
			At 293 K, mm/sec	
Fe(DPyTU)Cl_3	300	5.66	0.456	0.224
Fe(DPyTU)Cl_2	300	4.96	0.950	2.900
Fe(DPyTU)Br_3	301	5.96	0.368	0.384
Fe(DPyTU)$Br_2 \cdot 2H_2O$	302	4.83	0.980	0.750
Fe(DPyTU)$(NO_3)_3$	300	5.73	0.320	0.416
Fe(DPyTU)$(SCN)_3$	301	5.61	0.390	0.326
Fe(DPyTU)$(SCN)_2 \cdot 2H_2O$	300	5.14	0.850	0.625

[a] *IS* is given relative to $Na_2Fe(CN)_5NO \cdot 2H_2O$

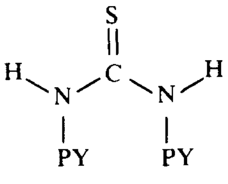
Likewise, for iron(III) complexes, the magnetic moment values indicate high spin variety; the reduced value of the magnetic moment suggests distortion from octrahedral structure, with considerable *pi* bonding. The isomer shifts for iron(III) complexes of DPyTU confirm that they are high spin type[22] for which the values lie in the range 0.3 to 0.45 mm/sec. The quadrupole splitting data also seem to underline this point.

Conformation of DPyTU

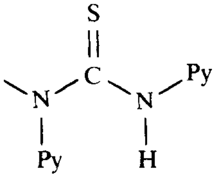
Three planar conformations are conceivable for DPyTU; the *cis-cis* form is least probable due to increased steric repulsion between the bulky pyridine rings. The results of the variable temperature NMR spectra in $CDCl_3$ reveal that at low temperatures (below 263 K), the spectra suggest an equilibrium mixture of *cis-trans* and *trans-trans* conformers. The ΔG value for C—N rotation as estimated from coalescence temperature is 13.5 kcal mol^{-1}.

CONCLUSION

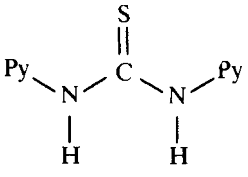
Molecular model shows that the bonding of DPyTU as a bidentate chelate through the two pyridine nitrogens is sterically unfavourable and would also then result in the least stable eight membered chelate ring. Bidentate chelation through ring nitrogen and thiocarbonyl sulfur and the bonding of the other pyridine nitrogen to a second metal atom is proposed. The geometry of DPyTU precludes tridentate chelation to the same metal atom. The solubility pattern and magnetic susceptibility values also suggest polymeric nature of the complexes. Tridentate coordination exhibited by DPyTU in contrast to bidentate chelation shown by the related ligands Py-X-Py (where X = S, SO_2, CO, etc.) should be attributed chiefly to the geometry of DPyTU; the increased distance between the two pyridine rings.



cis-cis



cis-trans



trans-trans

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