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Transition Metal Chemistry of Oxime-Containing Ligands, Part XIV. Iron(II) Complexes of *syn*-Phenyl-2-pyridylketoxime and *syn*-Methyl-2-pyridylketoxime

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Iron(II) complexes of the type $[\text{Fe}(\text{HL})_2\text{X}_2]$ (where HL = *syn*-phenyl-2-pyridylketoxime (Hppk) or *syn*-methyl-2-pyridylketoxime (Hmpk) and X = Cl^- , Br^- , I^- , NCS^- or NCSe^-) were synthesized and characterized by elemental analysis, molar conductance, molecular weight determination, X-ray powder diffraction patterns, magnetic susceptibility, Mössbauer, reflectance and IR spectral measurements. On the basis of these physical properties a halo-bridged dimeric *cis*-octahedral structure is suggested for the iron(II) halo complexes, whereas the remaining complexes appear to be monomeric with a *cis*-octahedral structure.

INTRODUCTION

Syn-Phenyl-2-pyridylketoxime and *syn*-methyl-2-pyridylketoxime have structural features in common with ligands of both the 2,2'-bipyridyl and the dimethylglyoxime types. In spite of this obvious interest in the properties of molecules possessing two distinct types of co-ordination site very little work has been reported¹ on complexes of Hppk and Hmpk. For iron(II) complexes studies have been mainly restricted² to complexes of pyridine-2-aldoxime (HpoX) and 6-methylpyridine-2-aldoxime (HmpX). In this paper, we report the synthesis and characterization by magnetic and spectral studies of iron(II) complexes of Hppk and Hmpk.

EXPERIMENTAL

Syn-Phenyl-2-pyridylketoxime (Hppk) and *syn*-methyl-2-pyridylketoxime (Hmpk) were prepared from 2-benzoylpyridine and 2-acetylpyridine (K & K Laboratories, New York) according to the method of Drago and Baucom³. The authenticity of the compounds was established by elemental analysis and physical properties [Hppk had m. p. 163—164 °C (Lit. m. p. 161 °C) and Hmpk, 121—122 °C (Lit. m. p. 121 °C) and IR spectra]. The anhydrous iron(II) salts, 2,2-dimethoxypropane (K & K Laboratories) and other organic solvents were of reagent grade.

Preparation and Analysis of Complexes

Dihalo-bis(syn-Phenyl-2-pyridylketoxime)iron(II), $[\text{Fe}(\text{Hppk})_2\text{X}_2]$ and *Dihalo-bis(syn-methyl-2-pyridylketoxime)iron(II)*, $[\text{Fe}(\text{Hmpk})_2\text{X}_2]$ (X = Cl^- , Br^- or I^-)

A solution of FeHal_2 (0.06 mole) in absolute EtOH (25 cm³) was prepared and kept under a stream of N_2 gas. A solution of Hppk or Hmpk (0.12 mole) in absolute

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EtOH (30 cm³) was prepared by heating while bubbling a rapid stream of N₂ gas through the solution. The metal salt solution was then added with stirring to the solution of the ligand under a N₂ gas atmosphere. A red colour formed immediately and a crystalline solid formed within minutes. The mixture was allowed to stand for 20 min under N₂ gas, then heated to boiling and filtered hot *via* suction through a sintered glass under N₂. The red crystalline solid was dried over P₄O₁₀ in vacuo.

Diisothiocyanato-bis(syn-phenyl-2-pyridylketoxime)iron(II), [Fe(Hppk)₂(NCS)₂] and *Diisothiocyanato-bis(syn-methyl-2-pyridylketoxime)iron(II)*, [Fe(Hmpk)₂(NCS)₂]

A solution of Fe(NCS)₂ (0.04 mol) in EtOH (25 cm³), prepared metathetically from FeCl₂ and KSCN, was added dropwise with stirring into a solution of Hppk or Hmpk (0.08 mol) in hot EtOH (20 cm³) and 2,2-dimethoxypropane (30 cm³). The solution mixture was boiled under reflux in an atmosphere of N₂ gas for 35 min. The dark red crystalline solid was collected by filtration in an atmosphere of N₂ gas, washed with EtOH and Et₂O and dried over P₄O₁₀ in vacuo.

Diisoselenocyanato-bis(syn-phenyl-2-pyridylketoxime)iron(II), [Fe(Hppk)₂(NCSe)₂] and *Diisoselenocyanato-bis(syn-methyl-2-pyridylketoxime)iron(II)*, [Fe(Hmpk)₂(NCSe)₂]

The procedure used in preparing these complexes was the same as used above except that, KSeCN was used in place of KSCN. The products isolated were intense red crystalline solids.

The iron content in the complexes was determined as Fe₂O₃, after igniting the complexes in air, and halides were determined by Volhard's method. The [SCN]⁻ and [SeCN]⁻ ions were estimated as silver thiocyanate and selenium metal respectively and carbon, hydrogen and nitrogen were determined microanalytically. The relevant data are given in Table I.

Physicochemical studies

Conductance measurements were made on a Toshniwal conductivity bridge type CLOI/OI. Molecular weights of complexes were determined cryoscopically. X-ray powder photographs were obtained using a Philips (Hungary) X-ray generator, nickel filtered copper radiation $\lambda = 1.5418 \text{ \AA}$ and Debye-Scherrer camera. Magnetic measurements from room temperature to 78 K were made on a standard Gouy's balance using CoHg(NCS)₄ as a calibrant. The diamagnetic corrections were estimated by using Pascal's constants¹. The room temperature magnetic moments are given in Table I.

Iron-57 Mössbauer spectra were recorded on polycrystalline samples by using a constant acceleration Mössbauer spectrometer. The spectrometer was equipped with a copper matrix source which was maintained at room temperature and was calibrated with natural iron foil. The low temperature results were recorded in a vacuum cryostat with a sample holder which protected the sample from the cryostat vacuum. The results were determined by inspection with an accuracy of ± 0.01 mm/s. The various Mössbauer parameters are given in Table III.

Diffuse reflectance spectra were recorded at room temperature on a Cary 14 spectrophotometer equipped with a reflectance accessory using MgO as a reference. The reflectance data are reported in Table IV. The IR spectra of Hppk and Hmpk and their complexes in the 4000—200 cm⁻¹ range were recorded in CsI on a Perkin-Elmer 337 spectrophotometer and far-infrared spectra in the range 400—100 cm⁻¹ were recorded on a Fourier spectrophotometer (FS-30). The relevant IR spectral data are given in Table II.

TABLE I
Analytical and Magnetic Moment Data for the Iron(II) Complexes

Compound	M. W. ^c	Found (Calc.) ^{10/0}	H	N	M	X	μ_{eff} , μ_B
		C					
[Fe(Hppk) ₂ (Cl) ₂] ^a	—	55.2 (55.1)	3.9(3.8)	10.75(10.7)	10.8(10.6)	13.7(13.6)	5.25
[Fe(Hppk) ₂ (Br) ₂]	—	47.2 (47.1)	3.3(3.3)	9.3 (9.1)	9.2 (9.1)	26.4(26.1)	5.26
[Fe(Hppk) ₂ (I) ₂]	—	40.96(40.8)	2.9(2.8)	8.2 (7.9)	8.3 (7.9)	36.4(36.0)	5.13
[Fe(Hppk) ₂ (NCS) ₂]	570.2(567.8)	50.86(50.7)	3.7(3.5)	9.9 (9.8)	10.2 (9.8)	20.6(20.4)	5.25
[Fe(Hppk) ₂ (NCSe) ₂]	667.4(661.8)	47.3 (47.1)	3.4(3.0)	12.8 (12.7)	8.6 (8.4)	24.2(23.9) ^d	5.21
[Fe(Hppk) ₂ (Cl) ₂] ^b	—	42.4 (42.1)	4.3(4.0)	14.4 (14.0)	14.3(14.0)	17.9(17.8)	5.23
[Fe(Hppk) ₂ (Br) ₂]	—	34.6 (34.4)	3.5(3.3)	11.6 (11.5)	11.6(11.4)	32.9(32.8)	5.20
[Fe(Hppk) ₂ (I) ₂]	—	28.9 (28.9)	2.9(2.7)	9.8 (9.6)	9.7 (9.6)	43.8(43.6)	5.10
[Fe(Hppk) ₂ (NCS) ₂]	448.0(443.8)	37.9 (37.8)	3.8(3.6)	12.76(12.6)	12.8(12.6)	26.4(26.1)	5.24
[Fe(Hppk) ₂ (NCSe) ₂]	549.7(537.8)	35.9 (35.7)	3.3(3.0)	15.9 (15.6)	10.5(10.4)	29.6(29.14) ^d	5.22

^a Hppk = syn-Phenyl-2-pyridylketoxime; ^b Hmpk = syn-methyl-2-pyridylketoxime; ^c Found (Calcd.) ^d X = Se

TABLE II
 Important IR Spectral Bands (cm^{-1}) and Their Assignments for the Iron(II) Complexes

Compound	ν (C—N)	ν (N—O)	ν (Py—I)	ν (Py—II)	ν (Py—III)	ν (Py—IV)
Hppk	1615(m)	980(vvs)	1580(vs)	1550(s)	1465(s)	1420(s)
[Fe(Hppk) ₂ (Cl) ₂] ₂	1620(m)	1050(s)	1590(vs)	1570(s, sh)	1470(s) 1460(vs)	1435(s)
[Fe(Hppk) ₂ (Br) ₂] ₂	1650(s, sh)	1067(s)	1590(vs)	1570(sh)	1470(s) 1460(vvs)	1440(vs)
[Fe(Hppk) ₂ (I) ₂] ₂	1647(s, sh)	1070(s)	1600(vs)	1570(w, sh)	1480(s) 1460(vvs)	1440(vs)
[Fe(Hppk) ₂ (NCSe) ₂] ₂	1650(s)	1054(s)	1590(vs)	1560(sh)	1472(s) 1450(vvs)	1440(vs)
[Fe(Hppk) ₂ (NCSe) ₂] ₂	1650(sh)	1060(vvs)	1600(vvs)	1565(sh)	1480(vs) 1460(vvs)	1442(vs)
Hmpk	1620(m)	980(vvs)	1575(vs)	1550(vs)	1460(s)	1425(s)
[Fe(Hmpk) ₂ (Cl) ₂] ₂	1648(m)	1060(vs)	1600(vs)	1570(vs)	1470(s) 1460(vs)	1440(s)
[Fe(Hmpk) ₂ (Br) ₂] ₂	1645(s, sh)	1068(m)	1595(s)	1560(w)	1472(s) 1460(vvs)	1435(vs)
[Fe(Hmpk) ₂ (I) ₂] ₂	1649(s, sh)	1070(s)	1590(vs)	1570(sh)	1475(s) 1460(vvs)	1440(vs)
[Fe(Hmpk) ₂ (NCS) ₂] ₂	1646(sh)	1070(vvs)	1600(vs)	—	1480(s) 1460(vs)	1442(s)
[Fe(Hmpk) ₂ (NCSe) ₂] ₂	1648(sh)	1070(vvs)	1600(vs)	—	1480(s) 1465(vvs)	1440(vs)

TABLE II Cont.

ν (C—H)	ϕ (C—C)	Ligand Absorption Bands	ν (Fe—X)	ν (Fe—N)ligand
788(s, b)	742(s)	400(vs, 335(s), 290(m), 270(w), 250(vs), 220(m), 185(s, b), 120(s, sh)	—	—
820(s)	775(s), 760(s)	400(vs), 339(s), 305(sh), 295(w), 280(m), 250(m), 220(w), 185(m), 125(s)	235(m), 215(m) 170(w)	370(m), 355(m) 320(s), 280(m)
820(s)	775(s), 760(s)	400(vs), 332(s), 302(sh), 295(w), 280(m), 248(m), 220(w), 187(m), 127(s)	140(w) 110(w)	370(m), 350(m) 315(m), 278(m)
815(m)	775(s), 760(m)	398(s), 330(s), 305(sh), 290(m), 280(s), 250(m), 220(m), 185(m), 120(m)	—	370(s), 352(s) 318(m), 280(w)
800(w)	740(vvs)			
820(s)	775(s), 758(m)	400(s), 335(s), 300(sh), 290(m), 275(m), 250(s), 220(m), 185(m), 125(m)	320(s), 240(m) 205(m), 165(w)	370(m), 350(s) 314(m), 280(w)
800(sh)	745(vvs)			
820(s)	775(s), 758(m)	398(vs), 332(m), 295(m), 270(m), 250(m), 220(m), 190(s), 125(s)	300(vs), 245(m) 208(m), 160(w)	370(s), 350(m) 315(sh), 280(m)
804(sh)	745(vvs)			
780(s)	740(s)	400(vs), 330(s), 292(m), 270(w), 254(s), 224(s), 180(s), 125(w)	—	—
818(s)	775(s), 760(m)			
800(w)	748(m)	400(vs), 335(m), 295(m), 275(m), 250(w), 225(m), 182(m), 125(s)	230(m), 215(m) 165(w)	368(s), 350(m) 320(s), 280(w)
820(s)	770(s), 760(s)	395(s), 330(s), 297(m), 270(w), 250(m), 220(s), 185(m), 125(m)	135(w) 108(w)	370(vs), 349(w) 318(m), 218(s)
800(w)	745(m)			
820(s)	770(s), 760(s)	400(vs), 335(s), 292(m), 272(m), 248(m), 220(s), 185(m), 127(s)	—	370(vs), 349(w) 320(sh), 278(s)
800(w)	740(m)			
818(vs)	765(s), 758(m)	395(vs), 330(m), 295(m), 275(m), 250(m), 225(s), 185(m), 125(s)	320(s), 240(m) 210(m), 165(m)	370(vs), 350(m) 314(sh), 280(m)
800(m)	742(s)			
818(vvs)	768(s), 760(m)	400(vs), 335(m), 295(m), 270(m), 250(s), 220(s), 182(s), 120(w)	320(s), 238(m) 208(m), 170(w)	368(vs), 348(s) 310(sh), 280(m)
800(m)	740(s)			

TABLE III
Mössbauer Spectral Parameters for the Iron(II) Complexes

Compound	Temp. K	ΔE_Q mm/s	δ^a mm/s	Γ_1^b mm/s	Γ_2^b mm/s
[Fe(Hppk) ₂ (Cl) ₂]	78	3.27	1.172	0.29	0.28
	RT	3.14	0.998	0.26	0.24
[Fe(Hppk) ₂ (Br) ₂]	78	3.26	1.17	0.28	0.28
	RT	2.90	1.00	0.25	0.24
[Fe(Hppk) ₂ (I) ₂]	78	3.27	1.19	0.29	0.28
	RT	2.85	1.04	0.25	0.25
[Fe(Hppk) ₂ (NCS) ₂]	78	3.19	1.15	0.28	0.27
	RT	2.74	0.982	0.24	0.23
[Fe(Hppk) ₂ (NCSe) ₂]	78	3.19	1.167	0.29	0.28
	RT	2.80	0.976	0.24	0.24
[Fe(Hmpk) ₂ (Cl) ₂]	78	3.26	1.15	0.28	0.27
	RT	3.12	1.00	0.26	0.26
[Fe(Hmpk) ₂ (Br) ₂]	78	3.25	1.16	0.27	0.26
	RT	2.80	0.99	0.25	0.24
[Fe(Hmpk) ₂ (I) ₂]	78	3.27	1.16	0.28	0.26
	RT	2.80	1.00	0.26	0.26
[Fe(Hmpk) ₂ (NCS) ₂]	78	3.18	1.14	0.26	0.26
	RT	2.85	0.976	0.24	0.25
[Fe(Hmpk) ₂ (NCSe) ₂]	78	3.20	1.14	0.27	0.27
	RT	2.85	0.966	0.25	0.26

^a Relative to natural iron foil; ^b Full width at half-maximum of low-velocity line, Γ_1 and high-velocity line, Γ_2 .

TABLE IV
Reflectance Spectral Data (kK) of Free Ligand and Iron(II) Complexes

Compound	I	$\pi \longrightarrow \pi^*$ II	III	Fe(t_{2g}) $\rightarrow \pi^*$ (HL)	${}^5B_2 \rightarrow {}^5B_1$	${}^5B_2 \rightarrow {}^5A_1$
Hppk	34.5	37.9	41.5	—	—	—
[Fe(Hppk) ₂ (Cl) ₂] ₂	31.95	37.4	40.39	18.9	10.54	8.42
[Fe(Hppk) ₂ (Br) ₂] ₂	31.96, 32.59	37.48	40.39	18.95	10.75	8.45
[Fe(Hppk) ₂ (I) ₂] ₂	31.00, 32.04	37.54	40.40	18.91	10.84	8.446
[Fe(Hppk) ₂ (NCS) ₂]	31.00, 32.02	37.53	40.37	19.0	11.96	—
[Fe(Hppk) ₂ (NCSe) ₂]	31.08, 32.00	37.61	40.40	19.2	11.97	—
Hmpk	34.48	37.03	40.00	—	—	—
[Fe(Hmpk) ₂ (Cl) ₂] ₂	30.20, 31.36	36.50	39.40	18.95	10.62	8.50
[Fe(Hmpk) ₂ (Br) ₂] ₂	30.19, 31.10	36.58	39.51	19.0	10.86	8.55
[Fe(Hmpk) ₂ (I) ₂] ₂	30.26, 31.08	36.08	39.60	18.4	10.97	8.57
[Fe(Hmpk) ₂ (NCS) ₂]	30.32, 31.20	36.16	38.76,	18.59	12.00	—
			39.58			
[Fe(Hmpk) ₂ (NCSe) ₂]	30.27, 31.38	36.98	38.86	18.6	12.00	—
			39.78			

RESULTS AND DISCUSSION

The iron(II) ion on interaction with Hppk and Hmpk yields the complexes corresponding to the general formula $[\text{Fe}(\text{HL})_2\text{X}_2]$ (HL = Hppk or Hmpk and X = Cl⁻, Br⁻, I⁻, NCS⁻ or NCSe⁻). All the complexes are quite stable at room temperature and do not show any sign of decomposition after a long period of standing. All the complexes are insoluble in water and non-polar solvents and except for iron(II) halo complexes, are partially soluble in moderate polar solvents and soluble in polar solvents. The molar conductance of $[\text{Fe}(\text{HL})_2\text{X}_2]$ (HL = Hppk or Hmpk and X = NCS⁻ or NCSe⁻) complexes in nitrobenzene and in ethanol (ca. 10^{-3} M) determined at 27° indicate their non-electrolytic behaviour⁵. Molecular weights of $[\text{Fe}(\text{HL})_2\text{X}_2]$ (HL = Hppk or Hmpk and X = NCS⁻ or NCSe⁻) in formamide show that they are monomeric.

The X-ray powder diffraction results suggest that isothiocyanate and isoselenocyanate complexes of the same ligand are X-ray isomorphous whereas halo complexes are not isomorphous with any one of the complexes mentioned above and hence are structurally different.

IR Spectra

The free ligands Hppk and Hmpk exhibit multiple bands in the 3300—2800 cm^{-1} range which are assigned^{1,2} to intermolecular hydrogen-bonded OH of the NOH groups. The $\nu(\text{C—H})$ stretching vibrations which could be presented in this region are obscured by $\nu(\text{OH})$ absorption bands. All Fe(II) complexes exhibit sharp intensity bands in the 3500—3400, 3200—3140, 3060—3040 and 2850—2840 cm^{-1} range which are assigned² to the free $\nu(\text{OH})$, hydrogen bonded $\nu(\text{OH})$, $\nu(\text{C—H})$, coupled $\nu(\text{OH})$ and overtone $\nu(\text{C=N})$ stretching vibrations, respectively. Hppk and Hmpk exhibit the $\nu(\text{C=N})$ acyclic and $\nu(\text{N—O})$ stretching vibrations at ca. 1610 and 980 cm^{-1} respectively. In Fe(II) complexes the $\nu(\text{C=N})$ acyclic and $\nu(\text{N—O})$ stretching vibrations are shifted towards the high frequency side and appear at ca. 1660 and ca. 1060 cm^{-1} respectively. These data clearly indicate⁶ that the oxime proton is not heterolysed and that there is a contribution from neutral $=\text{C=NOH}$ groups in these complexes. The coordination of the pyridine nitrogen atom to the iron(II) atom is indicated⁷ by shifting and splitting of the ring vibrations as is usually observed for other metal(II) complexes.

The N-bonded mode of coordination of thiocyanate and selenocyanate groups in $[\text{Fe}(\text{HL})_2\text{X}_2]$ (where HL = Hppk or Hmpk and X = NCS⁻ or NCSe⁻) complexes is confirmed⁸ by the presence of very strong split bands of ν_1 [$\nu(\text{C—N})$ stretching] at ca. 2100 and 2080 cm^{-1} . The observed splitting of the ν_1 vibration into two bands separated by ca. 20 cm^{-1} , is taken as an indication⁸ of *cis*- configuration. The ν_2 [$\delta(\text{N—C—S})$ or $\delta(\text{N—C—Se})$ bending] and ν_3 [$\nu(\text{C—S})$ or $\nu(\text{C—Se})$ stretching] vibrations are obscured by ligand absorption bands.

In iron(II) chloro complexes the bands at ca. 235(m) and ca. 215 cm^{-1} (w) are assigned to $\nu(\text{Fe—Cl})$ stretching vibrations and at ca. 170 cm^{-1} to $\nu(\text{Fe—Cl})$ bending vibrations. In the case of the iron(II) bromide complexes the bands due to $\nu(\text{Fe—Br})$ are weaker and appear at ca. 140 and ca. 110 cm^{-1} . The band due to $\nu(\text{Fe—I})$ is, as usual, weaker and no definite assignment of the $\nu(\text{M—I})$ is possible. The vibrations fall in the range expected⁹ for bridging

ν (Fe-halo) modes in C_{2v} octahedral geometry and therefore a halo bridged dimeric *cis*- octahedral structure is suggested for $[\text{Fe}(\text{HL})_2(\text{X})_2]_2$ complexes. In all the complexes four stretching bands of varying intensity associated with ν (Fe—N) ligand vibrations are observed at ca. 370, ca. 355, ca. 315 and ca. 280 cm^{-1} though ν (Fe—NCS) and ν (Fe—NCSe) stretching vibrations are also observed at ca. 320, ca. 240, ca. 210 and ca. 160 cm^{-1} in the ν (Fe—N) ligand vibration region. These assignments clearly suggest¹⁰ a *cis*- rather than *trans*-coordination of ligand molecules in these Fe(II) complexes.

Magnetic Behaviour

The Iron(II) complexes have room temperature magnetic moments in the 5.25—5.10 μ_B range which are essentially independent of temperature. The magnitude and temperature independence of the moments are reasonable for the distorted octahedral, high-spin iron(II) complexes¹¹.

Mössbauer Spectra

The iron(II) complexes exhibit Mössbauer spectra which are consistent with high-spin distorted octahedral iron(II). Both the quadrupole splitting ΔEQ and the chemical isomer shift, δ , decrease with increasing temperature. The quadrupole splitting parameter decreases from ca. 3.26 mm/s at 78 K to ca. 2.80 mm/s at 300 K. This behaviour is typical of distorted octahedral iron(II) complexes¹². The chemical isomer shift parameter decreases from ca. 1.19 mm/s to ca. 0.998 mm/s in the same temperature range. Such an increase in δ with decreasing temperature can be attributed to a second order Doppler shift arising from lattice effects¹³.

Reflectance Spectra

The diffuse reflectance spectra of iron(II) complexes have been measured at room temperature and are detailed in Table IV. The free ligands Hppk and Hmpk exhibit three intense transition bands at ca. 34.5, ca. 37.9 and ca. 41.5 kK; corresponding¹⁴ essentially to $\pi \rightarrow \pi^*$ transitions. The position of these bands and assignments are like those of 1.10 phenanthroline confirming the *cis*- form of Hppk and Hmpk in the solid state. The spectra of iron(II) complexes exhibit three intense bands in the 32.8—29.9, 37.6—35.8, and 40.4—38.8 kK region. The spectral bands are almost in the same position as in the *cis*-form of the free ligands, indicating the *cis*- conformation of the ligands in complexes in the solid state. The splitting of the first band of the order of ca. 1 kK suggests that it is vibrational in origins.

In iron(II) halide complexes the spectral bands observed in the 8.4—8.6 and 10.5—10.9 kK range are assigned¹⁵ to the ${}^5B_2 \rightarrow {}^5A_1$ and ${}^5B_2 \rightarrow {}^5B_1$ transitions respectively, which result from the splitting of the 5E_g excited state (O_h symmetry) in C_{2v} symmetry. It is apparent that the splitting of the 5E_g (O_h symmetry) is of the order of 2 to 2.4 kK in iron(II) halide complexes. The isothiocyanato and isoselenocyanato iron(II) complexes also exhibit the spectra typical of *cis*-octahedral complexes except that the splitting of the band system is not observed as is observed for iron(II) halide complexes. This situation is certainly consistent with the structure of these iron(II) complexes. In isothiocyanato and isoselenocyanato iron(II) complexes the iron(II)

atom is coordinated by six nitrogen atoms which substantially reduces the symmetry of the ligand field, more than the coordinated four nitrogen and two halogen atoms about the iron(II) atom in the iron(II) halo complexes. The iron(II) complexes also exhibit a very strong and broad band at ca. 19.0 kK which is assigned to $\text{Fe}(t_{2g}' \rightarrow \pi^*)$ (HL).

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SAŽETAK

Kemija kompleksa prijelaznih metala s oksimskim ligandima XIV. Kompleksi željeza (II) sa *syn*-fenil- i *syn*-metil-2-piridilketoksimom*Madan Mohan i Bhikari D. Paramhans*

Pripravljene su kompleksi željeza(II) s ligandima (HL): *syn*-fenil-2-piridilketoksimom i *syn*-metil-2-piridilketoksimom. Sastav tih kompleksa jest $\text{Fe}(\text{HL})_2\text{X}_2$ ($\text{X} = \text{Cl}^-$, Br^- , I^- , NCS^- , NCSe^-). Istraživanja raznim metodama (elementarna analiza, krioskopija, konduktometrija, rentgenska difraktografija praha, magnetokemijska mjerenja, refleksijska, IR i Mössbauerova spektroskopija) upućuju na zaključak da oni kompleksi u kojima je $\text{X} = \text{Cl}^-$, Br^- , I^- imaju dimernu *cis*-oktaedarsku strukturu s halogenskim premoštenjem; ostali pak istraživani kompleksi imaju monomernu *cis*-oktaedarsku strukturu.

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