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Five and Six Coordinated Complexes of Di and Trivalent Iron with Ligands Derived from Acidhydrazides and Acetylacetone

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Picolinic acid hydrazide(PH) and isonicotinic acidhydrazide (INH) react with acetylacetone in the presence of iron(II) and iron (III) salts and give complexes of open chain tetradentate ligands through a template effect. The complexes are isolated and characterised as five and six-coordinated by the help of analyses, conductance, molecular weight, magnetic, Mössbauer, electronic and infrared spectral studies. Two molecules of PH or INH condense with a single acetylacetone moiety giving open chain tetradentate ligands. Attempts to isolate the ligand in the free state are, however, unsuccessful. The $Ac(PH)_2$ coordinates through azomethine and pyridine nitrogens, while $Ac(INH)_2$ does so through azomethine nitrogens and amide oxygens. Mössbauer spectra are consistent with their proposed geometries and reveal that iron is in the high-spin state. Various ligand field parameters are calculated using normalised spherical harmonic Hamiltonian theory and the amount of distortion is calculated in terms of *DT/DQ*. Metal-ligand vibrations in the far IR region are discussed.

The transition metal chemistry of iron(II) and iron(III) complexes with phosphines and arsines is very extensive[1]; however, relatively few reports are available concerning compounds of pyridine based ligands[2-4]. Interestingly, a few iron(III) complexes exist as five coordinate monomers and bridged binuclear species[5] and among multidentate ligands, such cmplexes have recently been synthesised with pentadentate-ligands[6]. In general, Mössbauer spectra of iron compounds containing two or more metal atoms can provide evidence for the occurrence of structurally non-equivalent metal atoms and there have been several valuable applications of this technique. Although complexes of hydrazides and their hydrazones have been widely studied, no work apperas to have been done on the complexes obtained by the condensation of hydrazides and acetylacetone in the presence of various metal ions. The present paper deals with magnetic, Mössbauer, electronic and IR spectral studies of five and six coordinated complexes of iron(II) and iron(III) with $Ac(PH)_2$ and $Ac(INH)_2$.

EXPERIMENTAL

Ethyl-2-picolinate and isonicotinic acid hydrazides were obtained from Koch-Light and acetylacetone from BDH, England. All other reagents used were of reagent grade.

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Synthesis of Picolinic acid Hydrazide

The picolinic acid hydrazide(PH) was synthesised by refluxing ethyl-2-picolinate (0.10 mol) and hydrazine hydrate (99%) (0.10 mol) in a water bath for 4 h. The product obtained was recrystallised from ethanol m. p. $\approx$ 99.5 °C.

The acetylacetone picolinoyl(AcPH) and acetylacetone isonicotinyl(AcINH) monohydrazones were synthesised by refluxing methanolic solutions of picolinic(PH) or isonicotinic(INH) acid hydrazide (1.4 g) and acetylacetone (1.0 g) for 4 h in a water bath. The white solid obtained was recrystallised from methanol. The yield for acetylacetone picolinoyl monohydrazone (m. p. $\approx$ 230 °C) was poor (30%) while a 60% yield for acetylacetone isonicotinoyl monohydrazone (m. p. $\approx$ 255 °C) was obtained. For both compounds, elemental analyses and IR spectra show that acac is condensed to the NH_2 group of single hydrazide molecule and thus confirm the formation of acetylacetone monohydrazones of PH and INH.

Preparation of Complexes

Iron(II) sulphate or nitrate (10 mmol) dissolved in minimum quantity of water was diluted by 50 cm³ of methanol. Metal salt solution was added dropwise with constant stirring to the mixture of PH or INH (20 mmol) and acetylacetone (10 mmol). The reaction mixture was refluxed for 4 h and cooled. The crystalline precipitate was filtered, washed with ethanol, acetone, and ether and dried at 110 °C in an oven. Yield $\approx$ 30—40%.

Methanolic solutions of PH or INH (20 mmol), acetylacetone (10 mmol) and iron(III) salt (10 mmol) were mixed wtih constant stirring. The reaction mixture was refluxed for 5 h, when a syrupy liquid was obtained. It was kept in a refrigerator for 48 h, brown red crystals separated, were filtered off, washed with acetone, methanol, and ether and dried in a oven at 110 °C. Yield $\approx$ 30%.

For synthesising bromo and thiocyanato complexes, iron(II) sulphate and iron(II) nitrate were first treated with an excess of lithium bromide and ammonium thiocyanate, in order to generate the corresponding bromide and thiocyanate salts of iron(II) in solution.

The complexes are soluble in water and DMF but insoluble in other common organic solvents. They are stable up to 300 °C.

Magnetic and Spectral Measurements

The magnetic susceptibilities at room temperature were measured with a Gouy's balance using $[HgCo(CNS)_4]$ ($\chi_m = 51.65 \times 10^{-12}$ at 293 K) as calibrant. IR spectra in the range (4000—250) cm^{-1} were recorded in KBr pellets on a Perkin-Elmer-337 spectrophotometer. Far IR spectra (650—200) cm^{-1} were recorded in nujol-mull on a Beckmann IR-12 spectrophotometer. Iron-57 Mössbauer spectra were obtained using a 400 channel constant acceleration Mössbauer spectrophotometer equipped with a ^{57}Co source in a copper matrix. All the spectra were recorded at room temperature over a narrow range of $\pm$ 3 mm s^{-1} and the instrument was calibrated with sodium nitroprusside. Molar conductance was measured with a Toshniwal type CL01/01 conductivity bridge using a dip type cell. The molecular weights of the complexes were determined by Beckmann's cryoscopic method.

Iron was estimated with EDTA titrations using sulphosalicylic acid as indicator. The results were confirmed by titration with $KMnO_4$ after reducing Fe(III) to Fe(II) with stannous chloride. The microanalyses of C, H, and N were performed by Micro-analytical Division, C.D.R.I., Lucknow.

RESULTS AND DISCUSSION

The analytical data reported in Table I reveal the molecular formulae for the complexes to be $[Fe^{II}(L)X]$ and $[Fe^{III}(L)X_2]$, where L = $Ac(PH_2)$ or $Ac(INH)_2$ and X = Cl, Br, NO_3, or NCS. The conductance data show their non-electrolytic nature and the molecular weights (determined cryoscopically) are consistent with their proposed formulae. Tests for anions were positive only after decomposition of the complexes showing their presence in the coordination sphere.

TABLE I

Analytical and Magnetic Data of Iron(II) and Iron(III) Complexes

Complex	Colour	Found %					Calculated %				Halogen	B.M. μ_{eff}	Molecular weight
		M	C	H	N	Halogen	M	C	H	N			
$[Fe(C_{17}H_{17}O_2N_6)Cl]$	Light yellow	13.54	46.82	4.00	19.20	8.30	13.08	47.66	3.97	19.63	8.17	4.85	413
$[Fe(C_{17}H_{17}O_2N_6)Br]$	Greenish yellow	11.50	—	—	17.20	17.02	11.84	43.12	3.59	17.76	16.93	5.21	459
$[Fe(C_{17}H_{17}O_2N_6)NO_3]$	Greenish yellow	12.82	—	—	20.20	—	12.31	44.83	3.74	21.53	—	4.84	439
$[Fe(C_{17}H_{17}O_2N_6)NCS]$	Greenish brown	12.20	—	—	21.30	—	12.41	47.89	3.77	21.73	—	4.94	440
$[Fe(C_{17}H_{17}O_2N_6)Cl]$	Blackish brown	13.50	47.06	3.94	19.35	8.00	13.08	47.66	3.97	19.63	8.17	4.81	409
$[Fe(C_{17}H_{17}O_2N_6)Br]$	Brown	12.00	—	—	18.00	17.00	11.84	43.12	3.59	17.76	16.93	5.08	458
$[Fe(C_{17}H_{17}O_2N_6)NO_3]$	Dark-brown	13.00	—	—	21.80	—	12.31	44.83	3.74	21.53	—	4.90	435
$[Fe(C_{17}H_{17}O_2N_6)NCS]$	Chocolate brown	12.00	48.50	3.55	22.03	—	12.41	47.89	3.77	21.73	—	5.17	445
$[Fe(C_{17}H_{17}O_2N_6)Cl_2]$	Blackish brown	12.00	43.85	3.80	18.50	15.00	12.09	44.06	3.67	18.14	15.11	5.80	443
$[Fe(C_{17}H_{17}O_2N_6)Br_2]$	Dark-brown	10.00	—	—	15.80	28.20	10.12	36.88	3.07	15.19	28.93	5.93	536
$[Fe(C_{17}H_{17}O_2N_6)(NO_3)_2]$	Dark-brown	11.02	39.08	3.12	21.05	—	10.83	39.46	3.29	21.66	—	5.84	499
$[Fe(C_{17}H_{17}O_2N_6)(NCS)_2]$	Black	10.80	44.27	3.52	22.50	—	11.00	44.79	3.34	22.00	—	6.20	521
$[Fe(C_{17}H_{17}O_2N_6)Cl_2]$	Blackish brown	12.00	43.52	4.00	18.65	14.98	12.09	44.06	3.67	18.14	15.11	6.16	485
$[Fe(C_{17}H_{17}O_2N_6)Br_2]$	Black	10.52	—	—	14.98	28.28	10.12	36.88	3.07	15.19	28.93	6.07	530
$[Fe(C_{17}H_{17}O_2N_6)(NO_3)_2]$	Black	11.12	—	—	22.00	—	10.83	39.46	3.29	21.66	—	5.92	548
$[Fe(C_{17}H_{17}O_2N_6)(NCS)_2]$	Black	10.98	45.20	3.52	21.20	—	11.00	44.79	3.34	22.00	—	5.89	521

The magnetic moments of iron(II) complexes are in the range of $((44.5 \ldots 48.2)10^{-24}$ A m^2 per molecule. These values approach the range $(46.4 \ldots 51.0)10^{-24}$ A m^2 observed for the five coordinate complexes reported earlier[5,6]. The magnetic moments observed for iron(III) complexes, $(51.0 \ldots 57.5)10^{-24}$ A m^2 per molecule are well within the range reported for high-spin six coordinate iron(III) complexes[7].

The electronic spectra of iron(II) complexes exhibit the spectral bands $\approx 5400 \ldots 5550$, $\approx 8500 \ldots 8950$, $\approx 11200 \ldots 11900$ and $\approx 15900 \ldots 16350$ cm^{-1}. The spectral bands do not resemble those of four or six-coordinate, but are well within the range reported for five-coordinate complexes[8,9]. The bands above 15000 cm^{-1} arise from energy transfer which may be due to metal to ligand or ligand to metal transitions[10]. It is, however, difficult to differentiate between trigonal-bipyramidal or square pyramidal geometry, although the band ≈ 11000 cm^{-1} may be taken as evidence of square pyramidal stereochemistry[9]. A five-coordinate field splits into ^5E, $^5B_2$, $^5A_1$ and $^5B_1$ in C_{4v} symmetry thus, the bands ≈ 5500 and 11000 cm^{-1} may be assigned to $^5E \rightarrow {}^5A_1$ and $^5E \rightarrow {}^5B_1$, respectively[11,12]. The separation of $^5A_1$ and $^5B_1$, known for six-coordinate tetragonal complexes, is of the order of ≈ 3000 cm^{-1}. The presence of a single axial ligand would lead to a larger splitting of ^5E state than that of six-coordinate tetragonal complexes[13]. The splitting is of the order of ≈ 6000 cm^{-1} in the spectra of the present complexes and points towards the five-coordinate nature of these complexes.

The electronic spectra of Fe(III) complexes exhibit three typical d-d transitions in the regions $\approx 17300 \ldots 17700$, $\approx 19000 \ldots 19550$ and $\approx 24500 \ldots 24800$ cm^{-1}, and one broad band in the higher energy region ≈ 29000 cm^{-1}. The lower energy bands ≈ 17500 and 19500 cm^{-1} are probably due to a splitting of $^4T_{1g}$ term showing the distorted nature[14] of these complexes. The various bands can be assigned to $^6A_{1g} \rightarrow {}^4T_{1g}(E)$ (17300 ... 17700 cm^{-1}); $^6A_{1g} \rightarrow {}^4T_{1g}(^4A_2)$ (19000 ... 19550 cm^{-1}) and $^6A_{1g} \rightarrow {}^4T_{2g}$ (24500 ... 24800 cm^{-1}) and charge-transfer (29000 ... 30500 cm^{-1}), assuming D_{4h} symmetry. The value of $10Dq$ can only be determined indirectly, using the equation: $\Delta = f\,(\text{ligand}) \times g\,(\text{metal ion})$. The values of f (ligand) are calculated from values measured for chromium(III) complexes[14a] of the same ligands, using a value for g of 10.0[14]. In view of the tetragonal nature of the complexes, as expected due to the presence of donor atoms of unequal size and strength, the values of '*Dt*' are derived by splitting the first band which is equivalent to 35/4 *Dt*. The values of Dq^L and Dq^Z are also calculated (Table II). These values are used to determine the 'NSH' ligand field parameters[16]. The amount of distortion in terms of DT/DQ reveals that the complexes of $Ac(INH)_2$ are more distorted than those of $Ac(PH)_2$.

The Mössbauer spectra of $Fe^{II}Ac(PH)_2Cl$ and $Fe^{II}Ac(INH)_2Cl$ at room temperature exhibit isomer shift values (Table III) of 1.50 and 1.45 mm s^{-1}, respectively. These values are consistent with high-spin iron(II) with $S = 2$[17,18]. However, the possibility of magnetic crossover is ruled out because of the isomer shift is above the range suggested for these systems[19]. The value of ΔEQ for iron(II) complexes of $Ac(PH)_2$ and $Ac(INH)_2$ are 2.90 and 2.72 mm s^{-1}; these values are greater than 2.7 mm s^{-1} at room temperature, suggesting ground state splitting[20] in accordance with the results arrived at by the interpretation of their electronic spectra. The values of FWHM for $Ac(PH)_2$ and $Ac(INH)_2$ complexes of Fe(II) are 0.4582 and 0.3792 mm s^{-1} for left hand peaks

TABLE II

Electronic Spectral Data of Iron(III) Complexes

Complex	Spectral bands ν/cm^{-1}	Dq^{xy}	Dq^{z}	Dt	DT	DQ	DQ^{L}	DQ^{Z}	$\frac{DT}{DQ}$
[$FeAc(PH)_2Cl_2$]	17500, 19050, 24500	2105	1795	177	2401	55037	57878	49354	0.0436
[$FeAc(PH)_2Br_2$]	17700, 19550, 24680	2264	1895	211	2866	58859	62245	51471	0.0487
[$FeAc(PH)_2(NO_3)_2$]	17300, 19100, 24550	2175	1816	205	2788	56504	59804	49904	0.0493
[$FeAc(PH)_2(NCS)_2$]	17380, 19400, 24700	2287	1883	230	3129	59234	62937	51828	0.0528
[$FeAc(INH)_2Cl_2$]	17650, 19350, 24800	2090	1750	194	2634	54450	57460	48116	0.0484
[$FeAc(INH)_2Br_2$]	17580, 19400, 24850	2224	1860	208	2820	57784	61145	51110	0.0488
[$FeAc(INH)_2(NO_3)_2$]	17600, 19500, 24750	2234	1854	217	2944	57943	61420	50977	0.0508
[$FeAc(INH)_2(NCS)_2$]	17450, 19480, 24680	2264	1858	232	3145	58523	62240	51079	0.0536

TABLE III

Mössbauer Spectral Data of Iron(II) and Iron(III) Complexes (mm s^{-1})

Complex	Isomer shift (δ)	Quadrupale splitting (ΔEQ)	Peak positions		Full width at half maxima (FWHM)	
			L.H.P.	L.H.P.	L.H.P.	R.H.P.
[$Fe^{II}Ac(PH)_2Cl$]	1.51	2.90	0.0632	2.9704	0.4582	0.4108
[$Fe^{II}Ac(INH)_2Cl$]	1.45	2.72	0.0948	2.8124	0.3792	0.3634
[$Fe^{III}Ac(PH)_2Cl_2$]	0.60	0.82	0.1896	1.0112	0.6952	0.5688
[$Fe^{III}Ac(INH)_2Cl_2$]	0.58	0.79	0.1896	0.9796	0.5372	0.3950

and 0.4108 and 0.3634 mm s^{-1} for right hand peaks, respectively. These values again show that in [$Fe^{II}Ac(PH)_2Cl$], pyridine-nitrogen coordinates with the metal atom, while in [$Fe^{II}Ac(INH)_2Cl$] complexes, it does not do so[21].

The Mössbauer spectra of [$Fe^{III}Ac(PH)_2Cl_2$] and [$Fe^{III}Ac(INH)_2Cl_2$] at room temperature give values (Table III) for the isomer shifts (δ) of 0.60 and 0.58 mm s^{-1}, which are comparable with high-spin ($S = 5/2$) iron complexes having a configuration[22] of $t_{2g}^3\ e_g^2$. The values for quadrupole splitting (ΔEQ) are found to be 0.79 and 0.82 mm s^{-1}, which are in conformity with a high-spin ($S = 5/2$) nature for these complexes with a ground state $^6A_1$ [23]. The positive value of ΔEQ suggests that $Dq^{xy} > Dq^{z}$, wherein the equatorial field strength of the ligand is greater than the axial one[24] and is in conformity with the results arrived at by interpretation of the electronic spectra. The values of FWHM are 0.8532 and 0.5372 mm s^{-1} for left hand peaks and 0.7052 and 0.3952 mm s^{-1} for right hand peaks in [$Fe^{III}Ac(PH)_2Cl_2$] and [$Fe^{III}Ac(INH)_2Cl_2$] complexes, respectively are in accordance with the results arrived at by i. r. studies (vide infra), in the sense that in $Ac(PH)_2$ complexes pyridine nitrogen coordinates to the metal atom, giving rise to a larger value of FWHM compared with $Ac(INH)_2$ complexes, wherein pyridine nitrogen does not take part in coordination.[21]

Infrared Spectra

A comparison of the spectra of the free ligands with those of the $Ac(PH)_2$ complexes shows changes in the pyridine ring vibrations. The band I $\approx$ 1580 cm^{-1} shows an upward shift of 15 cm^{-1}, while the other two bands II and III, appearing at $\approx$ 1560 and 1470 cm^{-1}, show a downward shift of about 15 cm^{-1}. The ring breathing mode at $\approx$ 990 cm^{-1} increases in frequency and appears at $\approx$ 1005 cm^{-1}.[25] All these changes in pyridine ring vibrations point towards pyridine nitrogen coordination. The strong band $\approx$ 730 cm^{-1}, assignable to φ (C—C) disappears in the spectra of $Ac(PH)_2$ complexes, and new bands appear at $\approx$ 720 and 760 cm^{-1}. The C—C deformation vibrations designated as 6a and 16b modes at 610 and 410 cm^{-1} show an upward shift of 35—40 and 10—15 cm^{-1}, respectively. These changes also suggest that the pyridine nitrogen coordinates with the metal atom[26] in these complexes. However, the spectra of $Ac(INH)_2$ complexes do not exhibit such changes, ruling out any possibility of pyridine nitrogen coordination[26].

In the spectra of $Ac(INH)_2$ complexes, the amide I band appears at $\approx$ 1640 cm^{-1} showing a downward shift, the amide II band at 1540 cm^{-1} showing an upward shift, while the amide III band splits into two bands appearing at $\approx$ 1200 and 1380 cm^{-1}, respectively. The VI band shows an upward shift and appears at $\approx$ 500 cm^{-1}. All these changes are consistent with amide-oxygen coordination with the metal atom in these complexes[27]. Similar changes are, however, not observed in the spectra of $Ac(PH)_2$ complexes, indicating that amide oxygen does not coordinate in $Ac(PH)_2$ complexes.

The bands at $\approx$ 1630 and 840 cm^{-1} may be assigned to NH deformation coupled with OCN antisymmetric vibrations and NH out-of-plane bending, respectively[28]. These bands disappear in the spectra of the complexes and new bands appear at $\approx$ 1330 and 1280 cm^{-1}, respectively. These bands may be assigned to the amide group coupled with OCN stretching vibrations. The new sharp bands which appear in the spectra of the ligand at $\approx$ 1620—1610 and $\approx$ 1595 cm^{-1} may be assigned to ν(C=N) vibrations[29]. These bands in the spectra of all the complexes show a downward shift of 10—20 cm^{-1}, which indicates that azomethine nitrogen takes part in coordination. Thus, it appears that each acac. molecule has reacted with the amino group of two hydrazide molecules. This is analogous to the fact that one acac or even one acetone molecule reacts with the two available amino groups, forming ring closure, and giving rise to macrocyclic molecules[30]. This contention finds support in the presence of new bands in the spectra of the complexes at $\approx$ 2920, $\approx$ 1265, $\approx$ 1190 and 680 cm^{-1}, characteristic of the acac. moiety, and assignable to $\nu(CH_3)$, δ(Sym.CH_3), $\nu(C—CH_3)$, δ(CH) + $\nu(C—CH_3)$ and ring deformations, respectively. The absence of a strong band at $\approx$ 1530 cm^{-1}, characteristic of bonded carbonyl, further shows that both oxygen atoms of acac have reacted with two molecules of PH or INH, thus forming $Ac(PH)_2$ or $Ac(INH)_2$ species in the form of their metal complexes. Coordination with similar donor atoms in both sides of the molecules is indicated, since in the absence of such a coordination, the number of bands assigned to the various groups would have been doubled. It is clear from IR studies that though the isolation of the free tetradentate ligand is not feasible, its metal complexes are obtained by the reaction of hydrazides and acac in the presence of these metal salts.

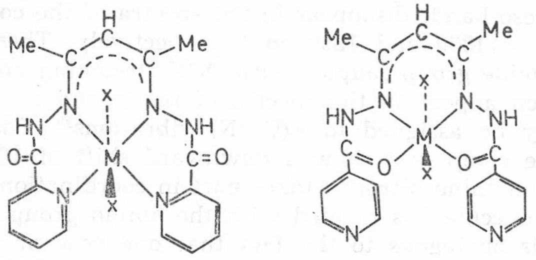
In the spectra of the nitrato complexes, the various bands observed at $\approx$ 1260, 1050 and 830 cm^{-1} are consistent with the presence and monodentate nature of the nitrate group[31]. Various $\nu(M—ONO_2)$ bands observed in the far IR support this coordination. The spectra of the thiocyanato complexes show various bands at $\approx$ 2130 cm^{-1} ν(CN), 820 cm^{-1} ν(CS) and 480 cm^{-1} NCS bending, respectively. These bands are characteristic of a monodentate N-bonded thiocyanate group[32].

Far IR Spectra

Far IR spectra of complexes of $Ac(INH)_2$ exhibit new bands at $\approx$ 415—420 cm^{-1}. These bands may be assigned to $\nu(Fe^{II}—O)$ and $\nu(Fe^{III}—O)$, respectively[33,34]. The absence of these bands in the corresponding complexes of $Ac(PH)_2$, further indicates that the amido-oxygen does not take part in coordination. The bands observed in the regions $\approx$ 265—270 cm^{-1} for Fe(II) and 255—260 cm^{-1} for Fe(III) complexes of $Ac(PH)_2$ may be assigned to the metalpyridine stretching vibrations[33]. All the complexes of iron(II) and iron(III) exhibit strong bands in the regions 385—390 and 370—375 cm^{-1} and may be assigned to metal-nitrogen (azomethine) stretching frequencies, respectively[29]. The vibrational modes observed in the regions 330—335 and 305 cm^{-1} may be assigned to $\nu(Fe^{II}—Cl)$ and $\nu(Fe^{III}—Cl)$, respectively[35]. In the thiocyanato complexes of

Ac(PH)$_2$, the ν(Fe^{II}—NCS) vibrations are observed at comparatively higher energy ($\approx$ 365 cm^{-1}). The ν(Fe^{III}—NCS) vibrations observable at $\approx$ 275 cm^{-1} with a shoulder on either side are consistent with the range reported for distorted octahedral thiocyanato complexes[36].

Based on magnetic, electronic Mössbauer and IR studies, the following structures may be proposed for these complexes:



where M = Fe^{II} or Fe^{III}, and X = Cl, Br, NO$_3$ or NCS.

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SAŽETAK

5- i 6-koordinirani kompleksi dvo- i trovaljanog željeza s ligandima izvedenim iz kiselinskih hidrazida i acetilacetona

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Hidrazidi pikolinske kiseline (PH) i izonikotinske kiseline (INH) reagiraju s acetilacetonom u nazočnosti željeza(II) i željeza (III) dajući komplekse novoga lančastog kvadridentatnog liganda u kojima je koordinacijski broj željeza pet ili šest. Ti su kompleksi bili izolirani i proučeni različiitm tehnikama (elementna analiza, konduktometrija, određivanje molne mase, određivanje magnetskih susceptibilnosti, elektronska i infracrvena spektroskopija te Mössbauerova spektroskopija).

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