Metal(II) Isoxazole Complexes: Spin Crossover in the Iron(II) Compounds

W. L. DRIESSEN* and P. H. van der VOORT

Gorlaeus Laboratories of the State University, P.O. Box 75, Leiden, The Netherlands

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A number of new solvates containing isoxazole as the ligand is reported, viz. [M(isoxazole)₆](BF₄)₂ (M is Mn, Fe, Co, Ni, Zn and Cd); [Fe(isoxazole)₆] (ClO₄)₂ and [Cu(isoxazole)₄](BF₄)₂(isoxazole). Ligand field spectra, magnetic moments and infrared data indicate that the bivalent metal ions, with the exception of copper, are octahedrally surrounded by the isoxazole molecules. Bonding occurs through the nitrogen atom. The iron complexes show a temperature dependent high spin–low spin transition.

Introduction

Many heterocyclic ring systems, like phenanthroline, pyrazole and thiazole are known to form stable complexes with various metal ions [1–4]. Bonding of these ligands to the metal ions occurs through the lone electron pair on the nitrogen atom. Not many coordination compounds have been reported with isoxazole as the ligand. A number of adducts $M(isoxazole)_nX_2$ where M is Co, Ni, Cu, and Cd, n = 1–2 and X is Cl⁻, Br⁻ and NCS⁻ have been reported by Cristini and coworkers [5]. Ponticelli *et al.* [6] reported some Pt(II) and Pd(II) adducts with 3,5-dimethylisoxazole. In this paper the preparation and characterization of a number of metal(II) solvates of isoxazole is reported, among which two iron complexes which show a temperature dependent high spin–low spin transition. In the literature a number of iron(II) compounds have been described which show the same behavior. However, in none of these compounds are the iron(II) ions surrounded exclusively by monodentate ligands of one type: these compounds contain bidentate, tridentate or tetradentate ligands, while in a number of cases the anions are also bonded to the iron(II) ions [7–13]. The surroundings of the iron(II) ions in these compounds thus deviate from a regular octahedron.

Experimental

The hexakis(aquo)metal(II) fluoborates were prepared from hydrofluoboric acid and the corresponding metal carbonates or hydroxides. Iron(II) perchlorate was commercially available. Isoxazole was prepared from hydroxylamine and 1,1,3,3-tetramethoxypropane [14].

The complexes were prepared by dissolving the hydrated metal(II) salt (0.005 mol) in a mixture of 5 ml nitromethane and 4 ml acetic acid anhydride, after which the ligand (0.04 mol) was added. Upon standing crystals separated, which were filtered off and washed with sodium-dried pentane. Drying *in vacuo* could not be carried out as loss of ligand resulted. The use of nitromethane as the solvent and acetic acid anhydride as the dehydrating agent gave better results than the use of ethanol and triethylorthoformate [15], for in the latter the compounds appeared to be contaminated with alcohol. All compounds are rather sensitive to moisture.

Metal analyses were carried out complexometrically as described by Schwarzenbach [16]. Carbon, hydrogen and nitrogen analyses were carried out by Mr. Buis of the TNO-Institute, Utrecht. Most of the compounds showed loss of ligand after a few days, the iron fluoborate compound even after some hours. Recrystallization of this compound from a mixture of nitromethane and isoxazole (20%) resulted in a less labile compound.

X-ray powder diagrams of the compounds were obtained with a Guinier type powder camera and Cu-Kα radiation. The samples were mounted with vaseline and protected from atmospheric vapour by adhesive tape.

Infrared spectra were recorded as nujol mulls between CsBr disks on a Beckman IR-10 spectrophotometer (4000–250 cm⁻¹) and as nujol mulls between polythene plates on a Grubb–Parson Cube interferometer (400–50 cm⁻¹). Diffuse reflectance spectra were obtained on a Beckman DK-2A ratio recording spectrophotometer in the 325–2500 nm region with magnesium oxide as reference.

Mössbauer measurements were performed on a constant acceleration spectrophotometer mounted with a 25 mC ⁵⁷Co source diffused into a 10 μm

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palladium foil. The correlation of the source to the sodium nitroprusside standard is 0.44 mm/s. The spectra were analysed (computer-fitted) on the presumption that they were build up of Lorenzian shaped lines (see Fig. 3), whereby the position of the low spin band was varied until an isotropic doublet — due to the high spin species — was obtained. The weak doublet, with i.s. = +1.47 mm/s and q.s. = 3.24 mm/s, appears to be due to a decomposition product. After prolonged evacuation of the iron compound (see above) this doublet increases in intensity, while at the same time the high spin doublet and the low spin band decrease in intensity.

Magnetic susceptibility measurements in the 293–85 K region were performed on a Gouy balance. The field was calibrated with $CoHg(CNS)_4$. Between 117 and 5 K measurements were taken with a PAR Parallel Field Vibrating Sample Magnetometer model 150 equipped with a calibrated GaAs diode. Magnetic susceptibilities were corrected for diamagnetism and temperature independent paramagnetism [17].

Results and Discussion

In Table I the compounds are listed together with their analytical results, melting points, colours, and X-ray types.

The X-ray diffraction patterns of the powdered compounds marked with A are very similar in d (Å) values and intensities. The same holds for the compounds marked with B. This indicates that isomorphism exists within these two groups of solvates. No similarities in the patterns of A, B, and C were observed.

The vibrational spectrum of isoxazole has been described and interpreted by several authors [18–20]. Since it is well known that some of the absorption bands of ligands shift upon complexation to metal ions [21], it was important to see whether or not such shifts occurred in our isoxazole complexes. It appeared that almost all absorption bands of the ligand shifted upon coordination with respect to the position of the corresponding bands in pure isoxazole

TABLE I. Metal(II) Complexes of Isoxazole (isox), Their Analytical Results (% weight), Melting Points (°C), Colours and X-ray Types.

	Metal(II)		Melting	Colour	X-ray
	Calc.	Found	Point[a]		Type
$Mn(isox)_6(BF_4)_2$	8.54	8.69	102 d.	Pale Pink	A
$Fe(isox)_6(BF_4)_2$ b	8.67	8.72	139 d.	Pale Purple–Blue	B
$Fe(isox)_6(ClO_4)_2$	8.34	8.40	120 d.	Purple–Blue	–
$Co(isox)_6(BF_4)_2$	9.11	9.09	179–183	Orange–Red	B
$Ni(isox)_6(BF_4)_2$ c	9.08	9.07	208–211	Violet–Blue	B
$Cu(isox)_5(BF_4)_2$	10.90	10.72	191 d.	Blue	C
$Zn(isox)_6(BF_4)_2$	10.01	9.93	134 d.	White	B
$Cd(isox)_6(BF_4)_2$	16.1	15.8	139–141	White	A

[a]d. = decomposes. [b]C: calc. 33.6, found 33.0; H: calc. 2.82, found 2.95; N: calc. 13.1, found 12.5. [c]C: calc. 33.4, found 33.8; H: calc. 2.78, found 2.76; N: calc. 13.0, found 12.8.

TABLE II. Some of the Infrared Absorption Bands (cm^{-1}) of Isoxazole (isox) and Its Metal(II) Complexes

	A1	A2	A3	A4	A5
	(ρ_{CH})	(ρ_{ring})	(ρ_{ring})	(ν_{MN})	(δ_{MN})
Isoxazole (liquid)	1028	916	845		
$Mn(isox)_6(BF_4)_2$	1032	938 (+22)	872 (+27)	225	–
$Fe(isox)_6(ClO_4)_2$	1034	940 (+24)	873 (+28)	–	–
$Fe(isox)_6(BF_4)_2$	1034	942 (+26)	875 (+30)	230	172
$Co(isox)_6(BF_4)_2$	1032	948 (+30)	880 (+35)	245	187
$Ni(isox)_6(BF_4)_2$	1032	954 (+38)	884 (+39)	265	210
$Cu(isox)_5(BF_4)_2$	1032	960 (+44)/916	889 (+44)/845	295	228
$Zn(isox)_6(BF_4)_2$	1032	953 (+37)	884 (+39)	260	–
$Cd(isox)_6(BF_4)_2$	1032	935 (+19)	876 (+31)	260	–

TABLE III. Absorption Bands (kK) in the Visible and Near Infrared, Their Assignments, the Calculated Ligand Field Parameters, and the Magnetic Moments of the Cobalt, Nickel, and Copper Isoxazole (isox) Complexes.

$Co(isox)_6(BF_4)_2$	10.4	$^4T_{2g} \longleftarrow ^4T_{1g}(F)$	Dq $= 1140$ cm^{-1}
	21.4	$^4T_{1g}(P) \longleftarrow ^4T_{1g}(F)$	B $= 815$ cm^{-1}
			μ(obs.) $= 4.74$ BM
$Ni(isox)_6(BF_4)_2$	11.35	$^3T_{2g} \longleftarrow ^3A_{2g}$	Dq $= 1135$ cm^{-1}
	13.15sh	$^1E_g \longleftarrow ^3A_{2g}$	B $= 845$ cm^{-1}
	18.18	$^3T_{1g}(F) \longleftarrow ^3A_{2g}$	
	28.57	$^3T_{1g}(P) \longleftarrow ^3A_{2g}$	μ(obs.) $= 3.00$ BM
$Cu(isox)_5(BF_4)_2$	14.9	$^2T_{2g} \longleftarrow ^2E_g$	μ(obs.) $= 1.77$ BM

(liquid). Most of the shifts were however not large (2–7 cm^{-1}) and were also not metal-dependent (see Table II, absorption band A1 as an example). Only two isoxazole absorption bands showed significant shifts, whose magnitudes depended on the metal(II) ion to which the ligand was bonded (Table II, bands A2 and A3). The order of the magnitudes of the shifts is: Mn < Fe < Co < Ni < Cu > Zn. This sequence is in accordance with the general order of stability found by Irving and Williams [22] for this kind of compounds, and which can be regarded as an electronegativety series. This behavior is in agreement with their assignment as ring deformation modes [18]. No splitting of ligand absorption bands has been observed, which indicates that the isoxazole molecules are bonded to the metal ions in the same manner and in a regular array.

The absorption bands A4 and A5 (Table II) could be attributed neither to ligand nor to anion vibrations and, moreover, these bands are metal-dependent in the Irving–Williams order [21, 22]. These 'new' bands must therefore be attributed to the species M(ligand)$_y^{2+}$ and can be ascertained as metal–ligand stretching, bending or wagging vibrations. The possibility of lattice modes can be ruled out, since absorptions due to such vibrations usually occur below 150 cm^{-1} in these kinds of compounds and such vibrations are also hardly or not metal-dependent [23]. We tentatively assign the A4 absorption band to the metal–ligand stretching vibration and the A5 absorption band to the metal–ligand bending vibration. These bands lie in the ranges in which metal–ligand stretching and bending vibrations of metal(II) complexes of other nitrogen-donor ligands usually occur [2, 23].

Absorptions due to anion vibrations have been observed at 1050 and 520 cm^{-1} for the BF_4^- ion and at 1090 and 620 cm^{-1} for the ClO_4^- ion. These observations, together with the absence of bands at about 750 and 350 cm^{-1} (for BF_4^-) and at about 930 and 455 cm^{-1} (for ClO_4^-), make it clear that the anions are not bonded to the metal ions [2]. The results described above justify the conclusion that our metal(II) complexes of isoxazole are true solvates. They must therefore be formulated as $[M(C_3H_3NO)_6]^{2+}$ (anion)$_2^-$, with the exception of the copper compound. In the infrared spectrum of the latter compound vibrations attributable to non-bonded ligand molecules are also present (see Table II, bands A2 and A3). This compound should therefore be formulated as $[Cu(isoxazole)_4]$ $(BF_4)_2$ (isoxazole).

The reflectance spectra of the cobalt and nickel compounds were typical for octahedral coordination of the metal ions. In Table III the positions of the absorption band and their assignments are given. From these values the ligand field parameters have been calculated, using the methods developed by Reedijk and coworkers [24, 25]. The Dq values lie in the range which is normal for nitrogen donor ligands, but appear to be high when compared with the Dq values of other heterocyclic monodentate nitrogen-donor ligands, as for instance imidazole [2]. The isoxazole molecules are thus coordinated to the metal ions through their nitrogen atom. As can be seen from Table III, the magnetic moments of the cobalt and nickel compounds lie within the range which is typical for octahedral coordination [26].

From the ligand field spectrum and the magnetic moment of the copper compound it cannot be deduced whether the copper(II) ion is in an octahedral, a tetragonally distorted octahedral, or a square planar environment. However, these data together with the analytical and infrared data suggest that the copper(II) ion is surrounded by four isoxazole molecules in a square, whereby the anions may (but then loosely) or may not be bonded in the axial positions.

The magnetic moment of the iron fluoborate compound drops from 5.25 BM at room temperature to 1.9 BM below 70 K. However, over a range of 40° (between 150 and 110 K) the magnetic moment of this compound has an 'intermediate' value of 3.2 BM, which eventually might be due to impurity of this compound. This is the reason why an iron complex with another anion has been synthesized:
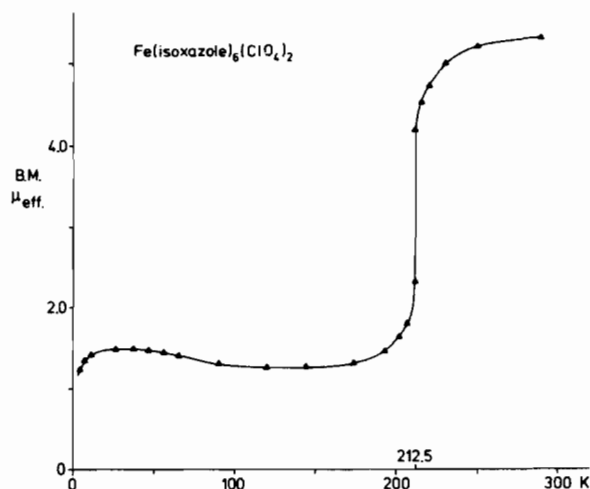
Figure 1. Temperature dependence of the magnetic moment of $Fe(C_3H_3NO)_6(ClO_4)_2$.

TABLE IV. Absorption Bands (kK) in the Visible and Near Infrared, the Magnetic Moments and the Mössbauer Data (mm/s) at Various Temperatures for the Iron(II) Perchlorate and Fluoborate Isoxazole Complexes.

$Fe(isoxazole)_6(ClO_4)_2$

T	σ_1	σ_2	σ_3	T	
293 K	11.8	18.2	26.7	273 K	μ(obs.) = 5.28 BM
90 K	12.0	19.1	27.6	180 K	μ(obs.) = 1.3 BM

T	q.s. HS	i.s. HS	i.s. LS
216 K	1.62 ± 0.03	1.35 ± 0.02	0.74 ± 0.02
204 K	1.64 ± 0.03	1.39 ± 0.02	0.71 ± 0.02
181 K	–	–	0.71 ± 0.02

$Fe(isoxazole)_6(BF_4)_2$

T	σ_1	σ_2	σ_3	T	
293 K	11.5	19.0	26.0	273 K	μ(obs.) = 5.25 BM
90 K	12.1	19.1	27.0	70 K	μ(obs.) = 1.9 BM

T	q.s. HS	i.s. HS	i.s. LS
233 K	1.36 ± 0.06	1.30 ± 0.04	0.66 ± 0.04
188 K	1.75 ± 0.06	1.35 ± 0.04	0.70 ± 0.03
90 K	–	–	0.77 ± 0.03

[Fe(isoxazole)$_6$] (ClO$_4$)$_2$. As can be seen from Figure 1, the magnetic moment of this compound drops sharply from 5.28 BM at room temperature to 1.3 BM below 180 K.

Infrared and X-ray data strongly suggest that in both compounds the iron(II) ions are in a regular octahedral environment: the iron fluoborate compound is isomorphous with the cobalt and nickel compounds, and the infrared spectra of both compounds showed no split absorption bands (see above). These are thus the first examples of compounds of

bivalent iron in a regular octahedral environment of monofunctional ligands which exhibit a high spin–low spin crossover.

The ligand field spectra of the iron compounds at room temperature contain three absorption bands attributable to electronic transitions (Table IV). On lowering the temperature, the relative intensity of σ_1 decreases, while the relative intensities of σ_2 and σ_3 increase (Figure 2). Obviously, σ_1 is an absorption band of high spin iron(II), to be assigned to the $^5E_g \longleftarrow {}^5T_{2g}$ transition, while σ_2 and σ_3 are
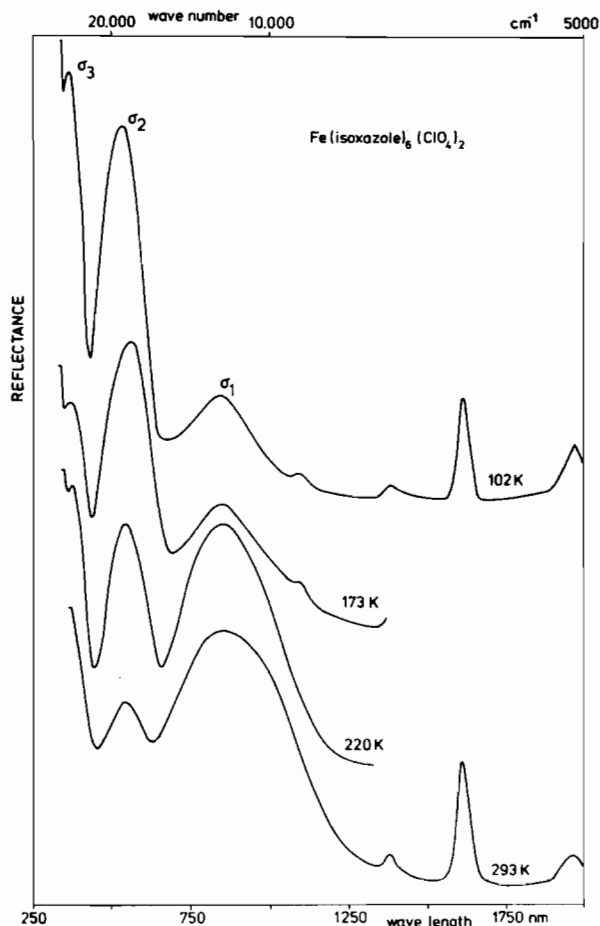
Figure 2. Reflectance spectra of $Fe(C_3H_3NO)_6(ClO_4)_2$ at various temperatures.

Figure 3. Mössbauer spectra of $Fe(C_3H_3NO)_6(ClO_4)_2$ at various temperatures.

associated with low spin iron(II). The latter may perhaps be assigned to respectively $^1T_{1g} \longleftarrow {}^1A_{1g}$ and the $^1T_{2g} \longleftarrow {}^1A_{1g}$ transitions.

The course of the electronic spectra with temperature shows that at room temperature the compound is not wholly high spin, while at low temperatures (T < 180 K) the compound is not wholly low spin. This is not in contradiction with the magnetic data, because the magnetic moment at room temperature is rather low for an octahedral high spin iron(II) compound, while the magnetic moment of the compound below 180 K is much too high for an octahedral low spin iron(II) complex [26]. However, the bulk of the high spin iron(II) is converted, within a short temperature interval, into the low spin species according to the magnetic behaviour of the compound (see Figure 2). The Mössbauer spectra (Figure 3) are also in agreement with the picture. The Mössbauer spectrum at 181 K consists of only one band, which indicates the presence of low spin iron(II) in a regular octahedral environment [27].
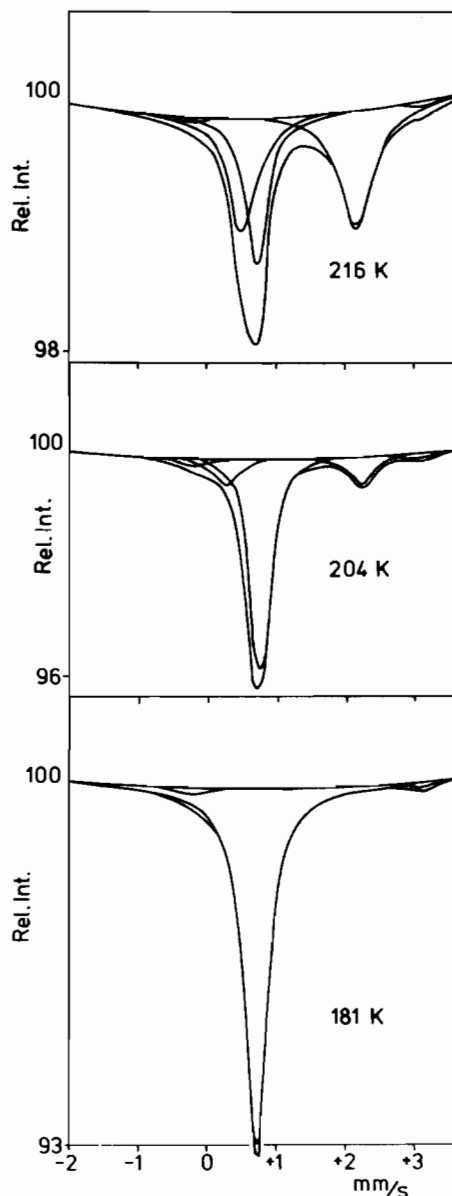
Conclusions

The present investigation has shown that isoxazole easily coordinates to bivalent metal ions, yielding hexa-solvates, except with copper in which the ligands are nitrogen-bonded. The iron compounds described in this work, which exhibit a temperature dependent high spin—low spin transition, are the first examples of such compounds in which the iron(II) ions are surrounded by a regular octahedral array of monodentate ligands.

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