1,2,4-Triazole Complexes, III*

Complexes of Transition Metal(II) Nitrates and Fluoroborates

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Transition metal(II) fluoroborates and nitrates give various complexes with 1,2,4-triazole. Most of these complexes are expected to be polynuclear. The infrared and ligand field spectra have been used to predict some structural aspects of the compounds. The iron complex shows a low spin → high spin transition on heating.

Introduction

Complexes of 1,2,4-triazole (trz) and of the 1,2,4-triazolate ion (trz′) have been described before. Most of the papers dealt with copper compounds, especially $CuCl_2(trz)$, $CuCl(trz')(H_2O)_2$ and $Cu(trz')_2$ [1–11]. Jarvis[12] determined the structure of $CuCl_2(trz)$. It is a polynuclear complex, the copper ions being bridged by two chloride ions and a 1,2-bicoordinating triazole ligand. The linear trinuclear structure of the complex

$Ni_3(NO_3)_6(trz)_6(H_2O)_8$

has been revealed by Reimann and Zocchi[13]. In this compound the nickel ions are linked by a triple bridge of 1,2-bicoordinating triazole ligands. Recently we investigated the also polynuclear complexes of composition $M(CNS)_2(trz)_2$ for M = Mn, Fe, Co, Ni, Cu, Zn[14, 15]. The infrared spectra of these compounds gave evidence for the 2,4-bicoordination mode of triazole. X-ray analysis confirmed this[16a]. One of the three types of monodentate coordination was discovered in the compound $MnSO_4(trz)(H_2O)_4$; the triazole ligands are 1-H,4-coordinating in this complex[16].

Investigations on transition metal(II) triazolates indicate that the triazolate ion may act as a bidentate or tridentate ligand[17].

In order to get an insight in the structure of metal complexes of 1,2,4-triazole, we studied the infrared and ligand field spectra of a number of such complexes, especially with fluoroborate and nitrate as anions. The aim of this study was to predict structural features on the basis of infrared and ligand field spectra.

Experimental

Metal salts and 1,2,4-triazole were obtained commercially; with exception of iron(II) fluoroborate which was prepared from iron and fluoroboric acid. In a few cases the metal salts had to be recrystallized from water. From most solvents with complexing properties triazole complexes separate as heteroligand complexes with solvent molecules. To minimize the effect of those ligands on the infrared spectra, we used water, or weakly complexing solvents as alcohols and ketones to avoid them at all. The complexes have been listed in Table I, together with their colours, preparation methods and analyses.

Preparation method A

5 mmol of metal salt were dissolved in 15 ml of ethanol and dehydrated with excess of ethyl orthoformate. This solution was added to a solution of 35 mmol of 1,2,4-triazole in 15 ml of ethanol. The complex precipitated immediately.

Preparation method B

Using the same amounts of metal salt and solvent as with method A, the salt was dissolved in water. This solution was added to a solution of 25 mmol of 1,2,4-triazole in water (B-1). Alternatively, a solution of 10 mmol of 1,2,4-triazole in water was added to the metal salt solution (B-2).

If a precipitate formed immediately after combination of the reactants, the mixture was heated and an amount of the appropriate acid, nitric or fluoroboric acid, was added until the precipitate

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* Part I see ref. 14, part II see ref. 15.

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Table I. Complexes of 1,2,4-triazole and some transition metal(II) nitrates and fluoroborates; preparation methods, colours and analyses (in %).

No.	Compound	Prep. meth.	Colour	Analyses							
				Experimental				Calculated			
				M	C	H	N	M	C	H	N
1	$\mathrm{CuBF_4(trz')(H_2O)_2}$	C 2	violetblue	25.4	9.8	2.3	17.2	25.0	9.4	2.4	16.5
2	$\mathrm{MnBF_4(trz')(trz)_2}$	B 1	white	16.2	20.8	2.6	35.7	15.8	20.7	2.3	36.2
3	$\mathrm{FeBF_4(trz')(trz)_2}$	B 3	pink*	16.2	20.4	2.6	35.8	16.0	20.7	2.3	36.1
4	$\mathrm{CuBF_4(trz')(trz)_2}$	C 1	blue	17.5	20.4	2.6	34.2	17.8	20.2	2.3	35.3
5	$\mathrm{ZnBF_4(trz')(trz)_2}$	B 1	white	18.4	20.0	2.4	34.7	18.2	20.1	2.3	35.2
6	$\mathrm{Ni(BF_4)_2(trz)_2(H_2O)_2}$	B 2	blue	14.3	11.8	2.6	19.9	14.4	11.8	2.5	20.7
7	$\mathrm{Ni(NO_3)_2(trz)_2(H_2O)_{8/3}}$	B 2	blue	15.6	13.0	3.2	29.9	15.9	13.0	3.1	30.3
8	$\mathrm{Cu(NO_3)_2(trz)_2}$	B 1	blue	19.4	14.7	2.3	32.9	19.5	14.8	1.9	34.4
9	$\mathrm{Mn(NO_3)_2(trz)_3(H_2O)_{3/2}}$	B 3	white	13.7	18.3	2.9	37.8	13.7	18.0	3.0	36.2
10	$\mathrm{Co(BF_4)_2(trz)_3(H_2O)_{5/2}}$	B 1	orange-yellow	11.8	15.4	2.3	26.3	12.2	14.9	2.9	26.0
11	$\mathrm{Ni(BF_4)_2(trz)_3(H_2O)_{\mathit{x}}}$	B 3	purple	variable composition							
12	$\mathrm{Cu(BF_4)_2(trz)_3(H_2O)_2}$	B 1	blue	14.8	15.6	2.9	25.0	13.2	15.0	2.7	26.3
13	$\mathrm{Zn(BF_4)_2(trz)_3}$	B 2	white	14.6	15.9	2.1	27.8	14.7	16.1	2.0	28.3
14	$\mathrm{Zn(NO_3)_2(trz)_3}$	B 1	white	16.2	18.2	2.6	38.3	16.5	18.2	2.3	38.9
15	$\mathrm{Mn(NO_3)_2(trz)_4}$	B 1	white	11.8	21.2	2.6	43.4	12.1	21.1	2.7	43.1
16	$\mathrm{Co(BF_4)_2(trz)_4}$	A	orange-yellow	11.4	19.6	2.9	33.7	11.6	18.9	2.4	33.0
17	$\mathrm{Co(NO_3)_2(trz)_{7/2}(H_2O)}$	A	orange	13.5	18.8	3.0	38.8	13.3	19.0	2.9	39.6
18	$\mathrm{Ni(BF_4)_2(trz)_4}$	A	light-violet	11.5	20.6	2.6	34.3	11.5	18.9	2.4	33.1
19	$\mathrm{Ni(NO_3)_2(trz)_4}$	A	light-violet	12.6	20.8	2.8	41.6	12.8	20.9	2.6	42.7
20	$\mathrm{Cu(NO_3)_2(trz)_4}$	C 1	blue	13.7	20.5	2.6	41.9	13.7	20.7	2.6	42.3

* This complex shows a low-spin → high-spin transition at 105–107 °C and turns white at that temperature.

just dissolved. After standing several days the complex separated. If not, the solution was concentrated or acetone was added to effect precipitation of the complex. Eventually no acid was used in method B-1, but an immediate precipitate was dissolved by boiling the solution for several minutes (B-3).

Preparation method C

Using acetone as a solvent and adding the metal salt solution to 25 mmol of 1,2,4-triazole in acetone, the complex precipitated immediately (C-1). A gelatinous precipitate formed when 10 mmol of 1,2,4-triazole in acetone were added very carefully and under stirring to the metal salt solution (C-2).

Elemental analyses of carbon, hydrogen and nitrogen were carried out by the analytical section of TNO, Utrecht, The Netherlands. The metal analyses have been done by complexometric titration. The infrared measurements were carried out with a Perkin Elmer Model 580 Infrared Spectrophotometer in the region of 4000–180 cm^{-1}. The samples were measured in Nujol mulls between KRS-5 windows. In the region below 300 cm^{-1} polyethylene windows were used. The ligand field spectra were recorded on a Beckmann DK 2A UV-Vis-spectrophotometer in the region of 2000–350 nm.

Table II gives the ligand field spectral data of the Fe, Co, Ni and Cu complexes. Figs. 1–7 give the infrared spectra of some representative complexes.

Table II. Ligand field spectra of 1,2,4-triazole complexes.

No.	Compound	Band positions in kK			
1	$\mathrm{CuBF_4(trz')(H_2O)_2}$	16.8			
3	$\mathrm{FeBF_4(trz')(trz)_2}$	19.3	~ 11.8 sh		room temperature
		~ 20 sh	12.9	11.0	at about 110 °C
4	$\mathrm{CuBF_4(trz')(trz)_2}$	15.9	9.5		
6	$\mathrm{Ni(BF_4)_2(trz)_2(H_2O)_2}$	26.3	17.5	10.9	
7	$\mathrm{Ni(NO_3)_2(trz)_2(H_2O)_{8/3}}$	28.4	17.8	10.9	
8	$\mathrm{Cu(NO_3)_2(trz)_2}$	16.6	11.3 sh		
10	$\mathrm{Co(BF_4)_2(trz)_3(H_2O)_{5/2}}$	21.7	19.7 sh	10.9	
11	$\mathrm{Ni(BF_4)_2(trz)_3(H_2O)_{\mathit{x}}}$	29.4	18.4	11.5	
12	$\mathrm{Cu(BF_4)_2(trz)_3(H_2O)_2}$	16.2	~ 10 sh		
16	$\mathrm{Co(BF_4)_2(trz)_4}$	21.3	10.6		
17	$\mathrm{Co(NO_3)_2(trz)_{7/2}(H_2O)}$	21.1	10.1		
18	$\mathrm{Ni(BF_4)_2(trz)_4}$	28.6	18.2	11.3	
19	$\mathrm{Ni(NO_3)_2(trz)_4}$	28.6	17.9	11.0	
20	$\mathrm{Cu(NO_3)_2(trz)_4}$	16.7			

Discussion

As was pointed out before[14], there is a striking difference between the infrared spectra of 4-H,1,2-coordinating triazole and 1-H,2,4-coordinating triazole. The main differences of course arise because of the selection rules of the local symmetry point group of the ligand.

The infrared spectrum of 1,2,4-triazole therefore, is a powerful tool to decide whether the molecule is 1,2-coordinating or not. If the absorption of the first ring torsion vibration is absent or strongly reduced in intensity, the triazole ligand possesses C_{2v} symmetry and will be 1,2-coordinating. For 2,4-coordination the molecule has C_s symmetry and one has to except two ring torsion vibrations to be active in the infrared spectrum. The same is true for the three monodentate coordination modes. The presence of two torsional vibrations, however, is not conclusive for either monodentate or 2,4-bidentate coordination. As will be shown, two torsional vibrations may be active in the infrared spectrum, when the complex contains triazole together with triazolate ligands.

CuBF₄(trz′)(H₂O)₂

During the preparation of 4 (Table I) one obtains a dark blue solution when only half of the amount of triazole is added. So we expected the existence of a complex with very low ligand/metal ratio. Such a compound was obtained according method C2 (**1**, Table I).

The infrared spectrum of the complex (Fig. 1) turned out to be quite different from those of other triazole complexes and matched very well with the spectrum of $CuCl(trz')(H_2O)_2$, prepared according PAOLINI and GORIA[2]. INOUE and KUBO[11] suggest a cyclic trinuclear structure for the latter complex on the basis of their magnetic susceptibility measurements. As both complexes show identical EPR signals ($g = 2.04$ signals of low intensity suggesting strong copper-copper interaction) a structure close to that of $CuCl(trz')(H_2O)_2$ is most probable for **1**. A polymeric structure, however, is also consistent with the infrared spectrum.

The coordination number of the copper ions in the structure of $CuCl(trz')(H_2O)_2$ described by INOUE and KUBO is probably five: *i.e.* bidentate triazolate and monodentate water and chloride. The infrared spectrum of **1** gave no evidence for coordination of the fluoroborate ions. For this reason we expect a slightly distorted square planar coordination for the copper ions in **1**, which is very feasible both in a trinuclear cluster and in a linear polynuclear structure.

MBF₄(trz′)(trz)₂, M = Mn, Fe, Cu, Zn

The infrared spectra of the compounds of composition $MBF_4(trz')(trz)_2$ are similar, except for the far infrared region. Between 700 and 600 cm⁻¹ one finds two absorptions which may be assigned to ring torsions. It is not justified to assign a C_s symmetry on the basis of these two absorptions. In the first place because the composition of the compounds leads to triazole and triazolate ligands and we should therefore expect a complex spectrum. This indeed is true for the region 1600–700 cm⁻¹.

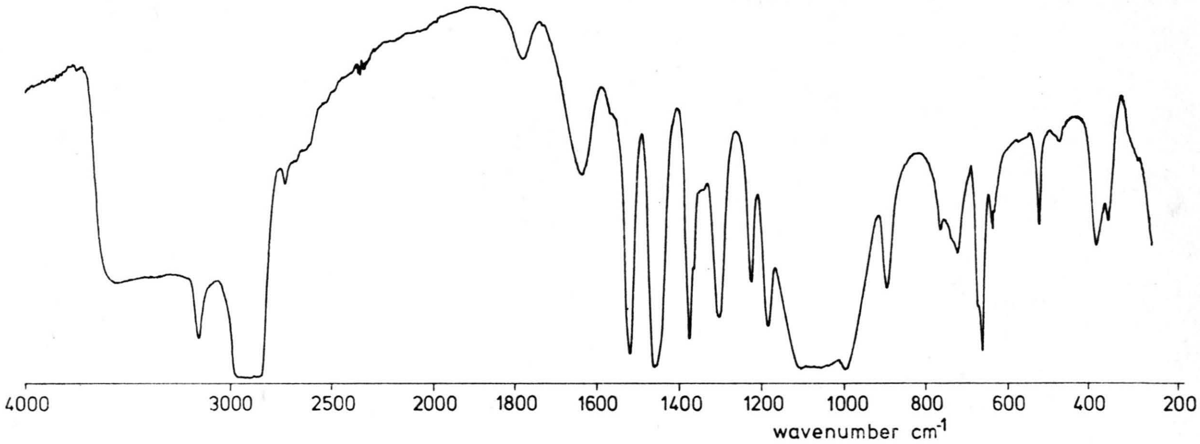

Fig. 1. Infrared spectrum of $CuBF_4(trz')(H_2O)_2$ (**1**) in Nujol, 4000–200 cm⁻¹.

Secondly, the separation of the two ring torsion absorptions is around 45 cm^{-1} which is larger than is expected for C_s triazole (about 34 cm^{-1} for the 2,4-coordinating triazole in $M(CNS)_2(trz)_2$ and 30 for monodentate triazole in $MnSO_4(trz)(H_2O)_4$).

So we arrive to the conclusion that the triazole ligands in the compounds **2**–**5** possess C_{2v} symmetry and are responsible for the absorption around 630 cm^{-1}. The triazolate ligands should be responsible for the other absorption around 675 cm^{-1}.

This last assignment agrees with the spectra of transition metal(II) triazolates[17] in which the infrared active ring torsion vibration can be assigned to the strong absorption around 670 cm^{-1}.

It is quite clear that if the above assignments are correct, the infrared spectra of the compounds **2**–**5** have to be composed of the spectra of the fluoroborate ion, the triazolate ion and the (C_{2v}) triazole. Therefore, we shall compare the infrared spectrum of one of these compounds, **5** (Fig. 2), with the triazole part of the spectrum of α-$Ni(CNS)_2(trz)_2$, a compound in which the triazole is undoubtedly C_{2v}[15], and with the spectrum of $Zn(trz')_2$. The result is given in Table III.

It can be seen that a rather good correlation exists. The assignment is proposed on the basis of the assignment for 1,2,4-triazole[20]. The conclusion is that the four compounds $MBF_4(trz')(trz)_2$, according to their infrared spectra contain triazole and triazolate ligands of which the former have C_{2v} symmetry. Coordination of the fluoroborate ions can be ruled out because there is no evidence for strong deviation from T_d symmetry for the BF_4^- groups. Although Table III shows that the triazolate part of the spectrum of $ZnBF_4(trz')(trz)_2$ matches the spectrum of $Zn(trz')_2$, it does not match the spectrum of the triazolate in compound **1**. It appears that there are at least two different types of infrared spectra for the triazolate ion. Undoubtedly, the differences in the spectra of which a closer examination will be published elsewhere[17], arise because of different coordination modes.

The reflectance UV-visible spectrum (Table II) of the copper compound (**4**) is of the type found for tetragonal distorted octahedral copper(II) complexes. It seems reasonable to assign to this complex a structure with the bidentate triazole ligands in the *x,y*-plane and the triazolate ligands bridging along the *z*-axis. The triazole ligands will probably be forced, for steric reasons, to lie with their molecular planes at an angle to the CuN_4-*x,y*-plane. The ligand field spectrum of the high-spin iron compound (**3**) too shows a distortion from pure octahedral symmetry. Considering the chemical composition, we again attribute this deformation to a tetragonal arrangement of the ligand donor atoms around the metal. A residual amount of low-spin complex probably is responsible for the weak shoulder at 20 kK in the spectrum of the high-spin compound; likewise, the shoulder at 11.8 kK in the low-spin spectrum is attributed to a residual amount of the high-spin. As the X-ray diffractograms indicate that the copper complex and the high-spin iron complex are both isomorphous with the low-spin iron complex and the zinc and manganese complexes, we assign a tetragonal arrangement to all complexes **2**–**5**.

The crossover point (T_c) was determined by differential thermal analysis. When warming up from room temperature with a heating rate of

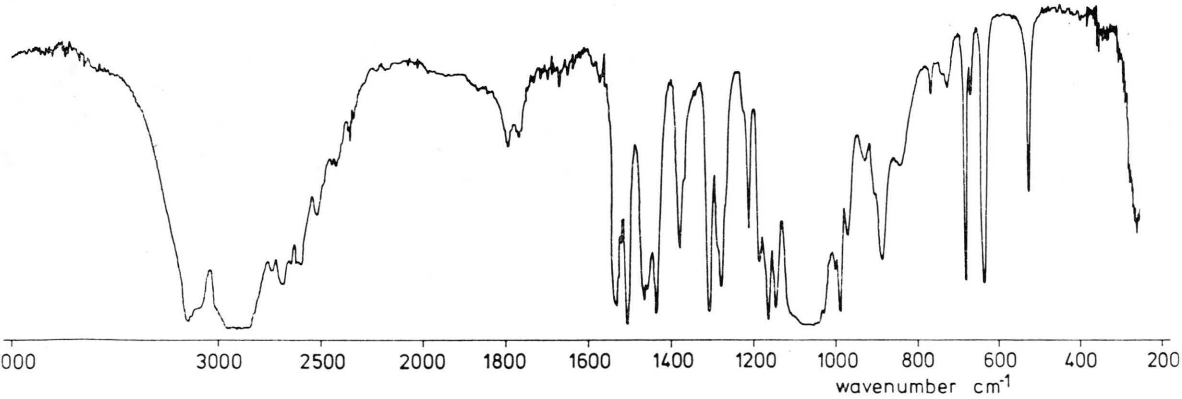

Fig. 2. Infrared spectrum of $ZnBF_4(trz')(trz)_2$ (**5**) in Nujol, 4000–200 cm^{-1}.

Table III. Infrared spectrum and assignment of $ZnBF_4(trz')(trz)_2$ compared with C_{2v} 1,2,4-triazole and triazolate. Combination bands, overtones and metal-ligand vibrations have been omitted. ν = stretching vibration, δ = in plane bending, γ = out of plane bending, ϱ = in plane ring vibration (stretching and bending) and τ = ring torsion vibration; ω are BF_4 vibrations.

Assignment	a-$Ni(CNS)_2(trz)_2$	$ZnBF_4(trz')(trz)_2$	$Zn(trz')_2$	Assignment
		3150 s	3135 s	ν(CH)
ν(CH)	3120 s	3130 m sh		
		3110 w sh	3115 w sh	ν(CH)
ν(CH)	3095 m	3095 m		
ν(NH)	~ 2950 s br	~ 2700 s br		
ϱ 1	1530 s	1534 s		
		1505 vs	1510 vs	ϱ 1
		1456 m	1422 s	ϱ 2
ϱ 2	1425 s	1437 vs		
ϱ 3	1380 mw	1345 w		
δ(CH)	1306 vs	1307 vs	1302 s	δ(CH)
		1279 vs	1268 vs	ϱ 3
ϱ 4	1225–1214 w doubl.	1225 w sh		
		1212 s	1211 s	ϱ 4
		1184 s	1150 vs	ϱ 5
ϱ 5	1150 s	1164 vs		
δ(NH)	1137 ms	1146 vs		
		1100 m br sh		ω 3 $^{10}BF_4$
δ(CH)	1071 vs	1080 m sh	1068 s	δ(CH)
		1060 vs br		ω 3 $^{11}BF_4$
		1026 m sh	1008 vs	ϱ 6
ϱ 6	1003 m	1000 m		
		988 vs	988 vs	ϱ 7
ϱ 7	958 m	969 s		
γ(CH)	893 s	928 m		
γ(CH)	882 w	904 w sh		
		886 vs	885 m sh	γ(CH)
		842 w	874 vs	γ(CH)
		768 w		ω 1 BF_4
γ(NH)	717 m	735 w		
		682 vs	688 w, 665 vs	τ 1 and τ 2
τ 1	676 vw	669 w		
τ 2	628 vs	635 vs		
		526 s		ω 4 BF_4
		353 vw		ω 2 BF_4

6°/minute, the spin transition occurred at 105 to 107 °C. Upon cooling from about 160 °C the reverse transition occurred at 73–76 °C.

The infrared spectra of the high-spin and low-spin iron complexes only differ in the region below 500 cm^{-1}. Two prominent absorptions in the low-spin spectrum shift to lower wavenumbers when the sample is heated to 110 °C. As is pointed out before[21], there are two electrons being transferred from an e to a t_2 orbital if T_c is approached from higher temperature and thus the transition should be followed by a decrease in the metal ion radius. Indeed, spectral evidence for *e.g.* $Fe(bipy)_2(CNS)_2$ [22] indicates stronger bonds in both the low-spin Fe–N(bipy) and Fe–NCS cases.

Our data support this. Assuming D_{4h} symmetry for the metal ion in compounds **2**–**5**, one has to expect two infrared active Fe–N stretching vibrations for **3**, one axial vibration of type A_{2u} and one equatorial vibration of type E_u. The vibration with the higher wavenumber probably is the Fe–N(trz′) stretching (A_{2u}) because metal-triazolate stretching vibrations are usually found at higher wavenumbers than metal-triazole stretchings.

As can be seen from Table IV the metal dependence of the vibrations is small and mainly influenced by the strength of the M–N bond according to the spectra of the Fe^{57} isotopic species. The lowest absorptions in Table IV around 200 cm^{-1} are probably from vibrations with a considerable amount of metal-ligand bending. Although D_{4h} symmetry may be suited to describe the ligand field spectra, it is questionable whether this symmetry is applicable to the infrared spectra. Perhaps D_{2h} is more adequate. D_{2h} would imply further splitting of the E_u vibration. This could not be observed,

Table IV. Metal-ligand absorptions of compounds $\mathrm{MBF_4(trz')(trz)_2}$.

Compound	Metal-ligand absorptions [$\mathrm{cm^{-1}}$]		
$\mathrm{MnBF_4(trz')(trz)_2}$	265 s	224 s	
$\mathrm{FeBF_4(trz')(trz)_2}$ l.s.	438 s (275 m)	301 s (262 m)	200 m
$\mathrm{FeBF_4(trz')(trz)_2}$ h.s.	277 vs	263 vs	198 m
$\mathrm{Fe^{57}BF_4(trz')(trz)_2}$ l.s.	435 s (274 m)	300 s (261 m)	198 m
$\mathrm{Fe^{57}BF_4(trz')(trz)_2}$ h.s.	276 m sh	262 vs	190 s
$\mathrm{CuBF_4(trz')(trz)_2}$	318 s	280 s, 273 m sh	213 m
$\mathrm{ZnBF_4(trz')(trz)_2}$	250 s	228 vs	205 m

however, although the spectrum of the copper complex is perhaps a sign of it.

In addition to the low-spin metal-ligand absorptions the spectrum of low-spin **3** shows also the two high-spin absorptions. This is not surprising because a certain percentage of high-spin species is present below $\mathrm{T_c}$ as was already demonstrated by the ligand field spectrum.

It is remarkable that the separation of the $\mathrm{A_{2u}}$ and $\mathrm{E_u}$ type M–N absorptions increases considerably upon going from high-spin to low-spin. The same effect has been observed for other compounds exhibiting spin-crossover, like $\mathrm{Fe(CNS)_2(bipy)_2}$. Although the conclusions of KÖNIG and MADEJA[23] were based upon an incorrect interpretation of shifts in CN vibrations[22], their suggestion that π-bonding plays an important role in these systems seems equally appropriate for **3**. To investigate this, however, would require more detailed structural information.

In addition to the absorptions of the iron complexes Table IV gives also the metal-ligand absorptions of the other complexes of formula $\mathrm{MBF_4(trz')(trz)_2}$.

Complexes with two triazole ligands per metal ion

The copper complex (**8**) has with the other compounds (**6** and **7**) in common that the triazole ligands show $\mathrm{C_{2v}}$ symmetry in the infrared spectrum (Fig. 3 compared with Fig. 4) and therefore are 1,2-bicoordinating. In the region of 1600–900 $\mathrm{cm^{-1}}$, however, considerable differences can be noted. Undoubtedly, the nitrate ions take part in the coordination of the copper ions, $\nu 3(\mathrm{NO_3})$ being split: 1462 and 1316 $\mathrm{cm^{-1}}$. According to KATZIN[18] such splitting is indicative for coordination.

In the nickel complexes (**6** and **7**) no such coordination of anions is present, the remaining coordination sites being provided with water ligands. Compound **7** is the well known trinuclear $\mathrm{[\{(H_2O)_3Ni(trz)_3\}_2Ni](NO_3)_6(H_2O)_2}$ [13].

As the spectra of **6** and **7** differ only for the anion vibrations, we assign to compound **6** this same trinuclear structure. Because there are some striking differences between the infrared spectra of **7** and **8**, especially in the 1150–950 $\mathrm{cm^{-1}}$ region, the assignment of the same structure to the copper complex seems unlikely. A polynuclear complex with the copper ions linked by double triazole

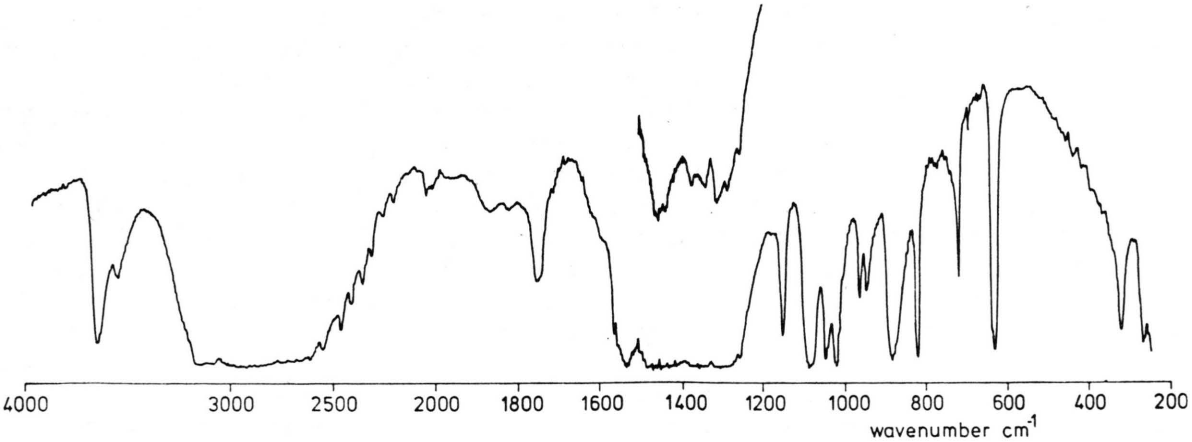

Fig. 3. Infrared spectrum of $\mathrm{Cu(NO_3)_2(trz)_2}$ (**8**) in Nujol, 4000–200 $\mathrm{cm^{-1}}$.

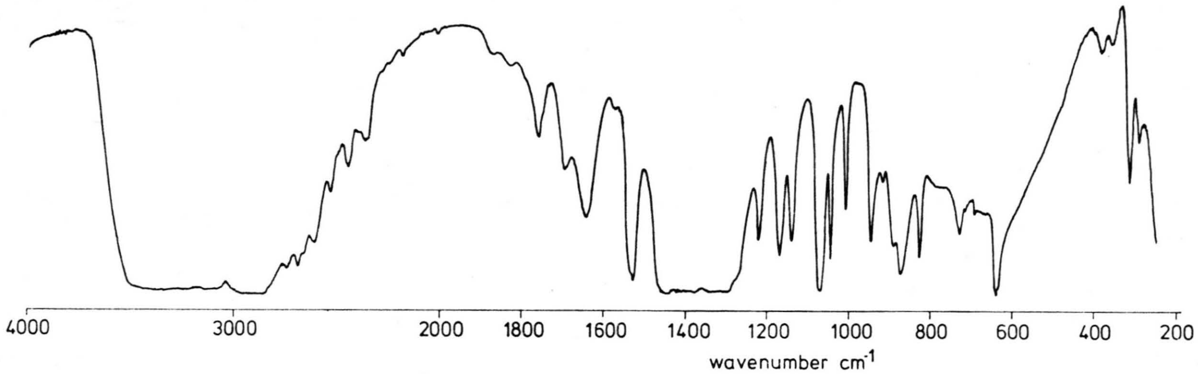

Fig. 4. Infrared spectrum of $Ni(NO_3)_2(trz)_2(H_2O)_{8/3}$ (**7**) in Nujol, 4000–200 cm^{-1}.

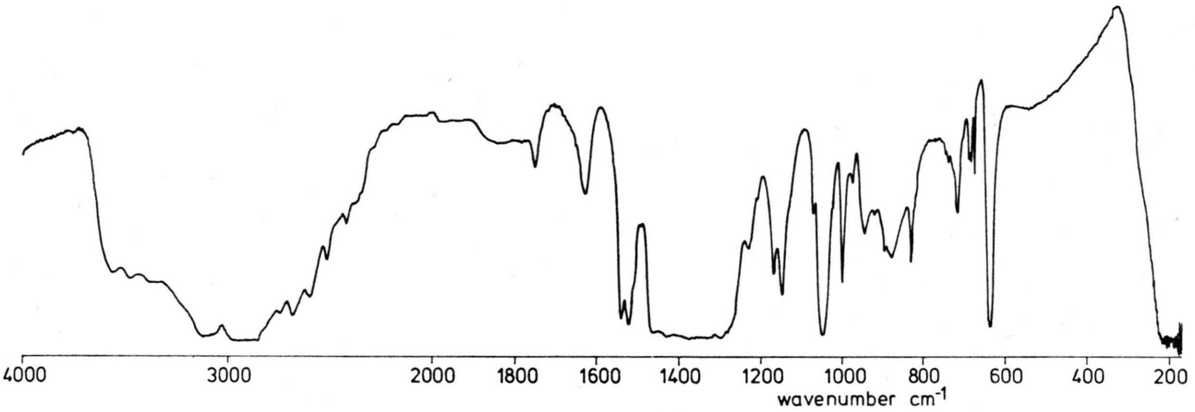

Fig. 5. Infrared spectrum of $Mn(NO_3)_2(trz)_3(H_2O)_{3/2}$ (**9**) in Nujol, 4000–200 cm^{-1}.

bridges is more probable. This would imply a tetragonally distorted octahedron for the coordination of the copper ions. The ligand field spectrum does not disagree with this.

Complexes with three triazole ligands per metal ion

All complexes with three triazole ligands per metal ion (**9–14**) show only one strong absorption in the 600–700 cm^{-1} region (Fig. 5). Again this indicates clearly C_{2v} symmetry for the ligand. It is not surprising to find these complexes matching in the other region of the spectrum as well. The structures of the complexes are probably polynuclear. Triply bridged metal ions in linear chains are possible.

The ligand field spectra of **10**, **11** and **12** reflect the six-coordination by triazole nitrogens. Assuming octahedral symmetry an assignment of these spectra can be made. Table V gives the Dq and B values calculated therefrom. This Table shows 1,2,4-triazole, when 1,2-coordinating, to be a very strong ligand. In the spectrochemical series it should be placed between ethylene diamine and bipyridyl, whereas in the nephelauxetic series it is comparable to dimethylformamide.

Table V. Dq and B values for tristriazolometal(II) complexes, assuming octahedral symmetry.

Compound	Dq [cm^{-1}]	B [cm^{-1}]	Dq/B
$Co(BF_4)_2(trz)_3(H_2O)_{5/2}$	1180	800	1.48
$Ni(BF_4)_2(trz)_3(H_2O)_x$	1150	905	1.27
$Cu(BF_4)_2(trz)_3(H_2O)_2$	1620		

In the far infrared region these complexes all show two prominent absorptions above 200 cm^{-1}, they are assigned to metal-nitrogen stretching vibrations and listed in Table VI.

Complexes with four triazole ligands per metal ion

Of the complexes with four triazole ligands only the copper complex has an infrared spectrum that is different from the other spectra, apart from the anion and metal-ligand vibrations (Fig. 6). More-

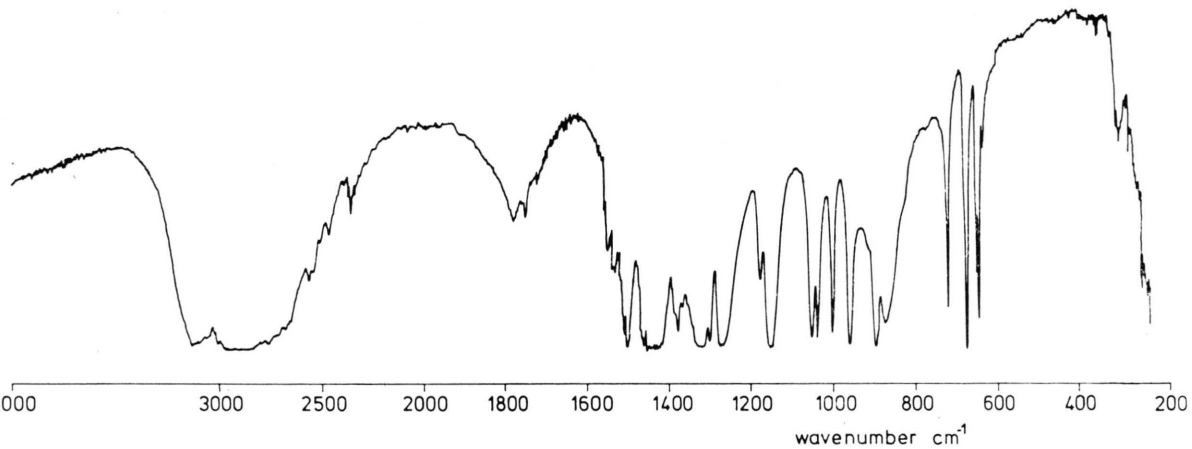

Fig. 6. Infrared spectrum of $Cu(NO_3)_2(trz)_4$ (**20**) in Nujol, 4000–200 cm^{-1}.

Table VI. Metal-ligand absorptions of tristriazolometal(II) complexes.

Compound	Metal-ligand absorptions [cm^{-1}]		
$Mn(NO_3)_2(trz)_3(H_2O)_{3/2}$	220 s	185 m	
$Co(BF_4)_2(trz)_3(H_2O)_{5/2}$	289 s	220 s	
$Ni(BF_4)_2(trz)_3(H_2O)_x$	310 s	246 m	
$Cu(BF_4)_2(trz)_3(H_2O)_2$	315 s	280 s	
$Zn(NO_3)_2(trz)_3$	255 m	230 s	215 s
$Zn(NO_3)_2(trz)_3$	230 s	215 s	

over, the strong 1365 cm^{-1} NO_3 absorption is split like in compound **8**: two strong absorptions at 1425 and 1315 cm^{-1}. These are assigned to coordinated NO_3 ions. Again, like with **8**, the splitting is larger than what would be expected for merely by steric reasons or hydrogen bridge formation perturbed nitrate ions[18]. The splitting is not as large as is usually met with bidentately coordinated nitrate[19].

In accordance with monodentately bonded nitrate, the rest of the spectrum of **20** shows clearly the presence of monodentately bonded triazole. Monodentate triazole is easily recognized in its spectrum because it resembles the spectrum of solid triazole more than do other complexes of triazole. In fact, the out of plane vibrations of the triazole ring in $MnSO_4(trz)(H_2O)_4$, of which the monodentate bonding has been proved[16], show up as a strong absorption at about 670 cm^{-1} and a medium strong absorption at 640 cm^{-1}. The difference with 2,4-bicoordinating triazole lies in the fact that this last absorption in 2,4-bicoordinating triazole is always found below 640 cm^{-1} and much more intense. Another difference offers one of the CH-bending vibrations. In all bidentate triazole spectra the absorption of this vibration is found around 1305 cm^{-1}. Solid triazole, however, has this absorption at 1272 cm^{-1} and $MnSO_4(trz)(H_2O)_2$ at 1282 cm^{-1}; **20** has it at 1276 cm^{-1} (the medium strong absorption at 1302 cm^{-1} is the first overtone of the lower ring torsion, compare solid triazole[20]).

Table VII gives the infrared spectra of monodentate 1,2,4-triazole in $MnSO_4(trz)(H_2O)_4$ and $Cu(NO_3)_2(trz)_4$ compared with the spectrum and assignment of solid 1,2,4-triazole[20]. The good agreement leads to the conclusion that in **20** the triazole has retained its 1-H tautomeric form and probably is 1-H,4-coordinating.

None of the other complexes with four triazole ligands show C_{2v} symmetry in its infrared spectrum because two torsion absorptions can be observed. Apart from the anion and metal-ligand vibrations the spectra of complexes **15–19** are quite similar. No significant indications for coordination by anions could be found.

The metal ions, therefore, are only coordinated by triazole ligands. An exception makes **17** in which part of the triazole ligands seems to be substituted by water. Even when a large excess of triazole was used the reaction between cobalt nitrate and triazole did not lead to a 1:4 complex. As the infrared spectrum of this compound was much alike to the spectrum of $Ni(NO_3)_2(trz)_4$ it is expected that either there was formed a mixture of compounds with a large amount of $Co(NO_3)_2(trz)_4$ or a structure was produced in which per two cobalt ions one triazole was substituted by two water ligands.

Table VII. Infrared spectra of monodentately coordinating 1,2,4-triazole, compared with the spectrum and assignment[20] of solid triazole.

Assignment	1,2,4-triazole	$MnSO_4(trz)(H_2O)_4$*	$Cu(NO_3)_2(trz)_4$** (Fig. 6)
ν(CH)	3123 m	3135 w	3135 s
ν(CH)	3116 m	3120 w	3100 m sh
ν(NH)	2730 s br	2720 m br	2760 s br
ϱ1	1531 s	1532 m	1536 m
ϱ2	1484 vs	1496 m	1505 s
ϱ3	1379 s	1383 m	1378 m
δ(CH)	1272 s	1282 s	1276 s
ϱ4	1258 s	1262 m	1270 m sh
δ(NH)	1181 s	1182 s	1178 m
ϱ5	1146 vs	1142 vs	1154 vs
δ(CH)	1058 vs	1060 s	1054 s
ϱ6	982 vs	986 s	1003 s
ϱ7	956 ms	962 s	961 s
γ(CH)	892 vw sh	894 m	896 s
γ(CH)	885 vs	872 m	873 m
τ1	684 vs	672 s	677 vs
τ2	651 vs	643 m	653, 648, 638 m

* Anion absorptions: 1120 vs, 1050 vs, 978 m, 621 ms, 616 ms,
** anion absorptions: 1435 vs, 1323 vs, 1039 s, 724 s.

The ligand field spectra of the nickel and cobalt complexes gave no reasons to speculate on another coordination than a pseudo-octahedron. The most simple way in which this can be accomplished by four triazole molecules is by two monodentate and two bidentate ligands.

The complex for which a confirmation of this expectation can be observed most clearly in the infrared spectrum is $Ni(BF_4)_2(trz)_4$ (**18**). Its spectrum (Fig. 7) shows that the absorption of the lower ring torsion is split and has a component at 652 cm^{-1}. There are four absorptions in the ring bending region 950–1000 cm^{-1} instead of two. There is an absorption around 1215 cm^{-1}, such absorption is always found for 1,2-bicoordinating triazole but not for 2,3-bicoordinating or monodentate triazole. The conclusion that **18** is a trinuclear complex like **6** and **7** having the water ligands substituted by monodentate triazole is in view of these findings not unrealistic. Magnetic measurements on this and other complexes may give further arguments for the structure of these complexes.

Conclusions

The infrared spectra of 1,2,4-triazole complexes can be used to discriminate between different modes of coordination. Triazolate ions that may take part

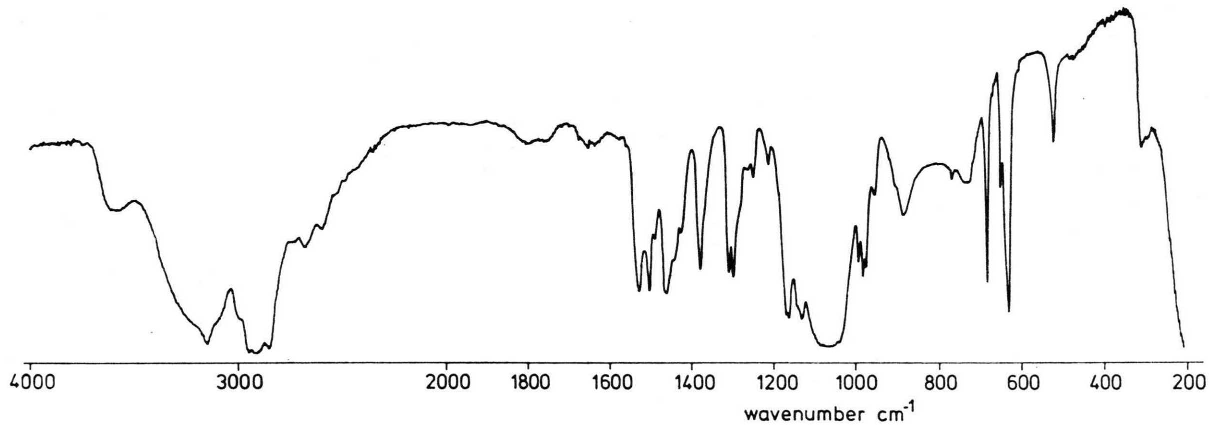

Fig. 7. Infrared spectrum of $Ni(BF_4)_2(trz)_4$ (**18**) in Nujol, 4000–200 cm^{1-}.

in the coordination are also easily recognized in the spectra. 1,2,4-Triazole, when bicoordinating, is a strong ligand and gives with iron(II) compounds low-spin complexes showing a spin transition at elevated temperature. One of such complexes has been described. It has a rather sharp transition point, although at room temperature both the infrared and ligand field spectra of the low-spin complex show the presence of a small amount of the high-spin complex.

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