Preparation, Spectroscopic and Magnetic Characterization of a New Series of Two-dimensional Transition Metal Compounds. The X-ray Structure of Poly-bis(thiocyanato-*N*)-bis-μ-[1,2,4]triazolo[1,5-*a*]pyrimidine-N^1,N^3)iron(II)

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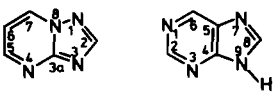
Abstract

The synthesis of a series of polynuclear compounds of general formula $[M(tp)_2(NCS)_2]_n$ (M = Mn, Fe, Co, Ni and tp = [1,2,4]triazolo[1,5-*a*]pyrimidine, $C_5H_4N_4$) is described. The compounds are X-ray and IR isostructural and were further characterized by ligand field and magnetic susceptibility measurements. The structure of the iron compound was determined by X-ray diffraction methods. It crystallizes in the orthorhombic space group *Aba*2, with $a = 8.028(2)$, $b = 20.422(6)$, $c = 10.129(5)$ Å. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares to $R = 0.040$ for 706 observed reflections. The structure consists of octahedral iron complexes in which the metal atom is coordinated by two nitrogen atoms from two monodentate NCS groups and by four nitrogen atoms from four symmetry-related tp molecules; each organic ligand bridges two metal atoms through both non-bridgehead triazole nitrogen atoms, joining the octahedral complexes in a layered system where the Fe···Fe distance is 6.49 Å.

Introduction

The coordination chemistry of 5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine has shown that this ligand coordinates to transition metal ions almost exclusively through its N_3 atom [1–3]. However, in some cases an adenine-type bidentate coordination mode was observed via its N_3 and N_4 atoms [4].

No evidence could be found for participation of N_1 in the coordination. In our studies on the coordination properties of azapurines we therefore turned to the unsubstituted [1,2,4]triazolo[1,5-*a*]pyrimidine, hereafter abbreviated as tp. This ligand is an isomer of purine by a shift of a pyrimidinic nitrogen to a bridgehead position. Below, the IUPAC numbering system for tp is compared with the biochemical numbering system for purine ligands. With the tp ligand it soon became clear that a great variety of compounds could be prepared with metal salts specific results depending critically on the reaction conditions. With metal thiocyanates in water a mixture of two crystal types was usually obtained, the composition of the mixture depending on the metal used, on the concentration and on the temperature. One component appeared to be free of solvent and with composition $M(tp)_2(NCS)_2$. The other component analyzed as $M(tp)_2(NCS)_2(H_2O)_2$; its preparation and properties are not further described in this paper. For the crystals of composition $M(tp)_2(NCS)_2$ a polynuclear metal compound may be expected on the basis of the formula. A structure determination was therefore desirable. The iron compound was chosen for this purpose, although suitable crystals of all the described compounds were available.



Scheme 1. (a) IUPAC numbering scheme of tp, (b) commonly used biochemical numbering of purine.

Polynuclear transition-metal compounds containing bridging heterocyclic ligands of biological implication are involved in relevant, natural electron-transfer reactions [5] and represent an interesting topic of magnetic exchange phenomena. Therefore the magnetic susceptibilities of the compounds were also measured and are described here.

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Experimental

Preparation

Metal salts for the preparations were reagent grade and used without further purification. tp was prepared from 3-amino-1,2,4-triazole and 1,1,3,3-tetramethoxypropane according to a described method [6]. The metal coordination compounds were prepared by adding ethanolic solutions of NH_4NCS (4 mmol in 10 ml) and tp (4 mmol in 10 ml) to an aqueous solution of metal nitrate (or sulfate in the case of iron) (2 mmol in 20 ml). Solutions standing at room temperature yielded flat, elongated crystals after several hours to several days. Occasionally, lump crystals of the hydrated compounds appeared as well. In such cases better results were obtained by dissolving all reactants in ethanol. By this method were prepared $Mn(C_5H_4N_4)_2(NCS)_2$, $Fe(C_5H_4N_4)_2(NCS)_2$, $Co(C_5H_4N_4)_2(NCS)_2$ and $Ni(C_5H_4N_4)_2(NCS)_2$. All compounds gave satisfactory elemental analyses for C, H, N and metal. They were isostructural from X-ray powder diagrams (using a Guinier type camera).

Physical Measurements

Ligand field spectra were taken on a Perkin-Elmer 330 UV–Vis–NIR spectrophotometer using MgO as a reference in the diffuse reflectance technique. Infrared spectra were recorded on a Perkin-Elmer 580B IR spectrophotometer as Nujol mulls between KRS-5 (Tl(Br,I)) and polyethene (below 400 cm^{-1}) and as CsCl-disks. Magnetic susceptibility data were obtained in the temperature range of 4–80 K on a PAR magnetometer Model 150A with the vibrating-sample technique, using $CoHg(SCN)_4$ as a reference compound.

X-ray Crystallography

An irregularly shaped yellow–green crystal was selected and mounted on the diffractometer. Crystal data and data collection parameters are given in Table I. Unit cell parameters were obtained by least-squares refinement of the θ values of 23 carefully centered reflections (with θ in the range 10–15°), chosen from diverse regions of the reciprocal space.

Data were collected at room temperature, the individual reflection profiles having been analyzed following Lehmann and Larsen [7]. The structure amplitudes were obtained after the usual Lorentz and polarization reduction. No correction for absorption was applied because of the low absorbance of the sample. Only the observed reflections were used in the structure solution and refinement.

Structure Solution and Refinement

The structure was solved by the heavy-atom method and refined by full matrix least-squares using the SHELX system of computer programs [8]. First isotropic and then anisotropic thermal parameters were estimated for the Fe, S and N atoms. In the final difference Fourier map all the four hydrogen atoms were clearly located and introduced in the final structure factor calculation with isotropic thermal parameters (mean values of those of the carbon atoms to which they are bound), but not refined. The function minimized during the refinement was $\Sigma w|\Delta F|^2$. Unit weights were chosen at each stage of the refinement after the variation of $|\Delta F|$ with respect to F_o was analyzed. The final R and R_w values were 0.040 and 0.045 ($R = \Sigma|\Delta F|/\Sigma|F_o|$) and $R_w = [\Sigma w(\Delta F^2)/\Sigma w|F_o|^2]^{1/2}$. A final difference map was featureless. Scattering factors used were taken from International Tables [9] with the exceptions of those of the hydrogen atoms, which were taken from ref. 10. Corrections for the real and imaginary components of anomalous dispersion were made for Fe and S atoms [9]. See also 'Supplementary Material'. Final atomic coordinates for the non hydrogen atoms are listed in Table II. The calculations were carried out on the Cyber 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale with the financial support of the University of Parma.

TABLE I. Experimental Data for the X-ray diffraction Study on the Complex $Fe(tp)_2(NCS)_2$

$C_{12}H_8FeN_{10}S_2$	
Crystal system	orthorhombic
Space group	$Aba2$
a (A)	8.028(2)
b (A)	20.422(6)
c (A)	10.129(5)
V (A^3)	1661(1)
Z	4
D_{calc} (g cm^{-3})	1.649
Molecular weight	412.23
Crystal dimensions (mm)	0.28 × 0.32 × 0.40
Linear absorption (cm^{-1})	11.66
Diffractometer	Siemens AED
Scan type	$\theta/2\theta$
Scan speed (° min^{-1})	3–12
Scan width (°)	$(\theta - 0.5) - [\theta + (0.5 + \Delta\theta)]$ $\{\Delta\theta = [(\lambda_{\alpha_2} - \lambda_{\alpha_1})/\lambda] \tan\theta\}$
Radiation	Nb-filtered Mo Kα ($\lambda = 0.7107$ A)
2θ range (°)	6–54
Reflections measured	(h, k, l)
Standard reflections	1 measured after every 50 reflections
Unique total data	962
Unique observed data [$I > 2\sigma(I)$]	706
No. of variables	83
R	0.040
R_w	0.045

TABLE II. Fractional Atomic Coordinates ($\times10^4$) with e.s.d.s in Parentheses for the Non-hydrogen Atoms

Atom	*x/a*	*y/b*	*z/c*
Fe	0	0	0
S	4772(3)	1370(1)	−79(6)
N	1688(9)	757(4)	−50(27)
N(3)	−1373(23)	1641(10)	1406(13)
N(5)	−3086(21)	1065(10)	2930(14)
N(7)	−3437(24)	434(10)	3275(16)
N(9)	−1558(24)	453(10)	1605(15)
C	2967(9)	1015(4)	−52(22)
C(1)	−3208(27)	2201(11)	2911(19)
C(2)	−1998(23)	2172(9)	1874(16)
C(4)	−1953(24)	1067(10)	1934(15)
C(6)	−3759(30)	1604(13)	3432(17)
C(8)	−2538(33)	98(4)	2471(20)

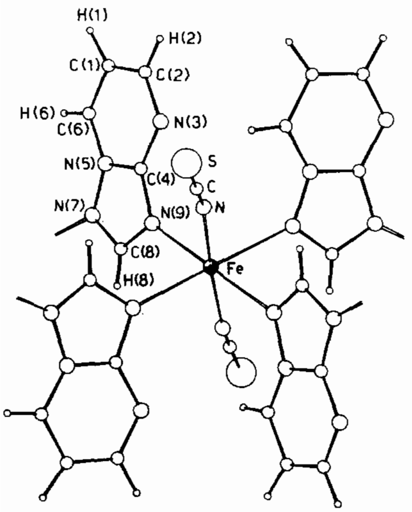

Fig. 1. View of the coordination around the iron atom with the atomic numbering scheme in $Fe(tp)_2(NCS)_2$.

TABLE III. Bond Distances (Å) and Angles (°)

(i) The coordination sphere of the iron atom			
Fe–N	2.056(8)	Fe–N(7^i)	2.33(2)
Fe–N(9)	2.25(2)		
N(9)–Fe–N	94.3(6)	N–Fe–N(7^i)	92.9(6)
N(9)–Fe–N(7^i)	94.9(7)	N–Fe–N(7^{iii})	85.0(5)
N(9)–Fe–N(9^{ii})	87.5(6)	N–Fe–N(9^{ii})	87.7(5)
N(9)–Fe–N(7^{iii})	177.4(6)	N–Fe–N^{ii}	177.2(11)
N(7^i)–Fe–N(7^{iii})	82.7(6)		
(ii) In the thiocyanate group			
N–C	1.15(1)	C–S	1.62(1)
Fe–N–C	158.4(7)	N–C–S	179.0(12)
(iii) In the organic ligand			
C(1)–C(2)	1.43(3)	C(6)–C(1)	1.40(3)
C(2)–N(3)	1.28(3)	C(4)–N(9)	1.34(3)
N(3)–C(4)	1.37(3)	N(9)–C(8)	1.38(3)
C(4)–N(5)	1.36(2)	C(8)–N(7)	1.29(3)
N(5)–C(6)	1.33(3)	N(7)–N(5)	1.36(3)
C(6)–C(1)–C(2)	117(2)	N(5)–C(4)–N(9)	110(2)
C(1)–C(2)–N(3)	125(2)	C(4)–N(5)–N(7)	109(2)
C(2)–N(3)–C(4)	116(2)	N(5)–N(7)–C(8)	103(2)
N(3)–C(4)–N(5)	121(2)	N(7)–C(8)–N(9)	116(1)
C(4)–N(5)–C(6)	124(2)	C(8)–N(9)–C(4)	101(2)
N(5)–C(6)–C(1)	117(2)	Fe–N(9)–C(4)	134(1)
		Fe–N(9)–C(8)	124(1)

Asymmetric units: *i* – ½ – *x*, *y*, –½ + *z*; *ii* –*x*, –*y*, *z*; *iii* ½ + *x*, –*y*, –½ + *z*.

Results and Discussion

In the crystal structure of $Fe(tp)_2(NCS)_2$ (Fig. 1) the iron atom, lying on a crystallographic two-fold axis, is planarly surrounded by four symmetry-related tp molecules, each of which coordinates to two metal atoms through both non-bridgehead triazole nitrogen atoms; the nitrogen atoms from two monodentate NCS groups in *trans* positions complete the octahedral environment around the iron atom. The relevant bond distances and angles are given in Table III. Whereas the Fe–N bond distance (2.056(8) Å) is one of the shortest found in octahedrally coordinated iron complexes with isothiocyanate anions (2.103(3)–2.156(11) Å [1c, 11, 12]), the Fe–N bond lengths involving nitrogen atoms from tp molecules are in the range 2.25(2)–2.33(2) Å, the last value being among the longest ones observed in octahedral iron compounds with ligands like tp [1c, 11, 13].

From the analysis of the planarity data the tp ligand is planar (the maximum deviation from the mean plane through the fused-ring system is 0.02(2) Å for C(8)); the π-electrons seem to be predominantly located on C(2)–N(3) and N(7)–C(8) bonds. The NCS group is linear, with bond lengths that suggest a partial sp^2-hybridization of the nitrogen and sulfur atoms, in good agreement with the value of the Fe–N–C angle (158.4(7)°) which deviates remarkably from the linearity as already found in a related thiocyanate iron(II) complex [11]. The bridging tp molecules join the octahedral complexes in a layered system, shown in Fig. 2, in which the tp molecules are tilted by 64° with respect to the equatorial plane containing the triazole nitrogen atoms from tp ligands.

The ligand behaviour of the NCS group and of the tp molecule differs from that found for the thiocyanate group and a dimethyl derivative (dmtp) in related compounds. In fact both in homo- [1a] and in heterometallic [1b,c] dmtp thiocyanate

TABLE IV. Comparison of Metal–Metal Distances and Magnetic Data of the Layered Compounds $M(tp)_2(NCS)_2$ and $M(trz)_2(NCS)_2$ [18, 19]

Metal	Ligand	Shortest intralayer M•••M (Å)	Shortest interlayer M•••M (Å)	Type of interaction	T_c (K)	$^aJ/k$ (K)	Ligand field maxima (cm^{-1})
Mn	tp	n.i.	n.i.	$S = 5/2, \theta = -9$ K	–	–0.39	n.i.
	trz	6.437	9.057	Heisenberg, $S = 5/2$	3.292	–0.25	n.i.
Fe	tp	6.460	10.970	$S' = 1/2, \theta = -13$ K	–	–6.5	7830; 11610
	trz	6.264	9.058	Ising, $S' = 1/2$	8.46	–7.2	11700
Co	tp	n.i.	n.i.	$S' = 1/2, \theta = -14$ K	–	–7.0	7580; 9620; 16980
	trz	6.239	9.049	XY, $S' = 1/2$	5.71	–5.0	10000; 20800
Ni	tp	n.i.	n.i.	$S = 1, \theta = -16.5$ K	–	–3.1	8730; 13480; 15630; 2626
	trz	6.168	9.053	Heisenberg, $S = 1$	10.14	–4.5	11000; 17500; 28200

n.i.: not investigated. [a]For tp complexes estimated using the molecular field relation from θ.

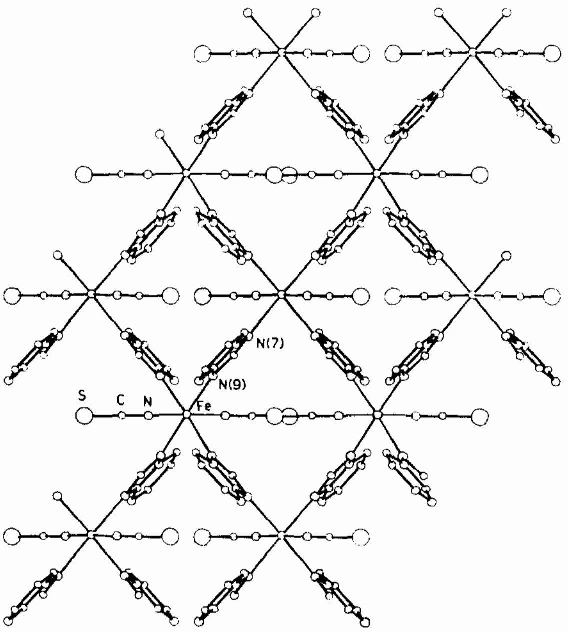

Fig. 2. Perspective view of a layer of complexes, lying in the (101) plane, in the structure of $Fe(tp)_2(NCS)_2$.

compounds, dmtp acts always as a monodentate ligand through the usually favoured triazole nitrogen atom (even if both non-bridgehead triazole nitrogen atoms are available for coordination) and the NCS anions act both as S-bound monodentate ligands and as bidentate bridges. As pointed out mainly about d^8 transition metal thiocyanate complexes, the bonding mode of the NCS group can be influenced by many factors and the balance of these factors is not easily understood [14]. In this compound the borderline acid character [15] of the Fe^{2+} cation seems to be such as to justify the *N*-bonding of the NCS anions as well as the *N,N*-bridging role of the tp molecules between the Fe atoms. In particular, in spite of the different steric demand, the bonding mode of the organic ligand is similar to that found for the histidine ligand in some natural dinuclear compounds e.g., in superoxide dismutase [16] in which the Cu•••Zn distance by EXAFS methods was found to be 6.30 Å. In $Fe(tp)_2(NCS)_2$ the analogous Fe•••Fe distance in the layers is 6.46 Å. The coordination mode of the ligand can even better be compared with that found for the less bulky 1,2,4-triazole, when acting as a 2,4-bridge, with borderline acids as Co^{2+}, Cu^{2+}, Zn^{2+} [17], Mn^{2+}, Ni^{2+} [18] and Fe^{2+} [11]. Table IV compares the intra and inter metal–metal distances of these last-mentioned compounds with those of $Fe(tp)_2(NCS)_2$; some magnetic and spectral properties are tabulated as well. The infrared spectra show that the compounds $M(tp)_2(NCS)_2$ with M = Mn, Fe, Co and Ni are mutually isomorphous, apart from the far-IR. In contrast to the thiocyanate complexes of dmpt [2], the NCS groups are in *trans* positions. This is reflected by the ν(CN) thiocyanate vibration (Table V) which occurs

TABLE V. Infrared Vibration Absorptions of the Thiocyanate Group of $M(tp)_2(NCS)_2$

Compound	ν(CN) (cm^{-1})	ν(CS) (cm^{-1})	δ(NCS) (cm^{-1})
$Mn(tp)_2(NCS)_2$	2060vs	785m	480ms
$Fe(tp)_2(NCS)_2$	2062vs	790m	485ms
$Co(tp)_2(NCS)_2$	2080vs	792m	489ms
$Ni(tp)_2(NCS)_2$	2091vs	791m	492ms
Range in $M(trz)_2(NCS)_2$ [19]	2075–2090	780–792	478–480
Range in *cis* $M(dmtp)_2(NCS)_2(H_2O)_2$ [2]	2090–2110	791–796	474–476

about 25 cm^{-1} lower than in the dmpt compounds for all the metals. In this respect the compounds are similar to those of 1,2,4-triazole $M(trz)_2(NCS)_2$ which are also layered compounds [18]. There is a difference, though, in the interactions among the layers. The layers in $M(trz)_2(NCS)_2$ are connected to each other by means of N–H···S hydrogen bridges [13]. In $M(tp)_2(NCS)_2$ this is not possible because tp has no NH group and the packing of the layers is realized by van der Waals contacts only. As a consequence of this the absorptions in the IR spectra of $M(tp)_2(NCS)_2$ are all rather sharp. From Table V, where the thiocyanate absorptions of the compounds $M(tp)_2(NCS)_2$ are compared with their range in the $M(trz)_2(NCS)_2$ compounds, it is clear that the two classes of layered structures can be correlated very well on the basis of similarities and dissimilarities in the crystal structure. Therefore, the question arises why the trz compounds show fairly large ordering temperatures (3–10 K) [18], whereas the tp complexes did not give significant anomalies in χ down to 4 K (Table IV). As the J/k values estimated from the Curie–Weiss temperature (region 20–80 K) by the molecular field relation $\theta = 2zJS(S+1)/3K$ [20], suggest that some interaction is present, we conclude that if ordering is present T_c is either below 4 K, or the type of interaction must be different. This last case implies for instance that $Fe(tp)_2(NCS)_2$ may not be an Ising type system. Detailed measurements of the susceptibilities at very low temperature and of the specific heat are in progress.

Supplementary Material

Atomic coordinates for the hydrogen atoms, thermal parameters and a list of calculated and observed structure factors are available from the authors on request.

Acknowledgements

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