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Spectral Properties and Crystal Structure of Bis(μ-thiocyanato-*N,S*)bis(thiocyanato-*N*)tetrakis(5,7-dimethyl[1,2,4]triazolo[1,5-α]pyrimidine-N^3)dicopper(II) and of Tetrakis(5,7-dimethyl[1,2,4]triazolo[1,5-α]pyrimidine-N^3)platinum(II) hexa(thiocyanato-*S*)platinate(IV)

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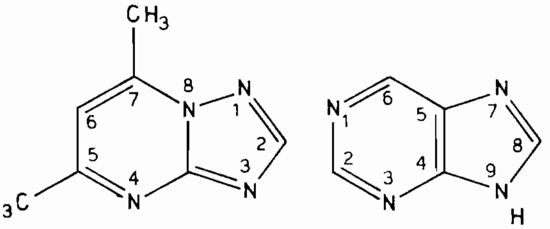
The preparation, spectroscopic studies and the crystal structure of $Cu(dmtp)_2(NCS)_2$ *(*I*) and* $Pt(dmtp)_4Pt(SCN)_6$ *(*II*) (dmtp stands for the 5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine ligand) are described. Crystals of* I *are monoclinic, space group* C2/c, *with* $a = 19.088(7)$, $b = 11.516(8)$, $c = 20.118(7)$ Å, $\beta = 104.51(4)°$, $Z = 28$; *crystals of II are monoclinic, space group* $P2_1/n$, *with* $a = 16.914(8)$, $b = 11.474(9)$, $c = 11.893(7)$ Å, $\beta = 91.52(4)°$, $Z = 2$. *The structures of* I *and* II *have been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares to* $R = 0.044$ *for* I *and* 0.051 *for* II. *The structure of* I *consists of centrosymmetric dimers* $[Cu(dmtp)_2(NCS)_2]_2$, *in which the copper atoms, bridged by two thiocyanate groups, are in a square pyramidal arrangement involving two isothiocyanate nitrogen atoms and two triazole nitrogen atoms from two dmtp ligands in the basal plane and a thiocyanate sulphur atom from the centrosymmetric complex in the apical position. The structure of* II *consists of square planar* $[Pt(dmtp)_2]^{2+}$ *cations, in which the platinum atom is bound to four triazole nitrogen atoms from dmtp ligands and of octahedral* $[Pt(SCN)_6]^{2-}$ *anions with the metal bound to sulphur atoms of thiocyanate anions.*

Introduction

An increasing interest is being devoted to the biological effects of heavy metals in the environment; in particular the interactions of metal ions, both natural ones like Cu^{2+} and toxic ones like Pt^{2+}, with nucleic acid fragments are extensively investigated.

Imidazole-type ligands are often present in this type of compounds. The 1,2,4-triazole shows a remarkable resemblance with imidazoles, although some differences appear in the coordination behaviour of the two types of ligands [1]. Studies on the naturally-occurring bases in DNA have revealed that the purine ligands prefer the imidazole N_9 atom for coordination, but the N_7 atom, when N_9 is blocked. Adenine acts as a bidentate ligand (coordinating through N_3 and N_9) in some copper(II) compounds [2].

In order to better elucidate the influence of the steric effects on the coordination, we have prepared and characterized some metal complexes using 5,7-dimethyl[1,2,4]triazolo[1,5-α]pyrimidine (hereafter abbreviated as dmtp) as a new ligand, a fused ring system differing from the purine skeleton mainly in having a pyrimidine nitrogen atom in a bridge-head position. The numbering system used is indicated below.



IUPAC numbering schemes of dmtp and purine molecules.

Metal thiocyanates of stoichiometry $M(dmtp)_2(H_2O)_2(NCS)_2$ have been obtained. In the structure

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of the Cd derivative determined by X-ray analysis mononuclear complexes are present, in which the coordination of the metal involves two dmtp ligands in the *trans* position (coordinated through N_3), two water molecules in the *cis* position, and two isothiocyanate ligands, also in the *cis*-position [3].

Three different copper(II) thiocyanate complexes have been isolated. Two of them are expected to be dinuclear on the bases of their ESR spectra. Crystals suitable for X-ray analysis have so far been obtained for the complex $Cu(dmtp)_2(NCS)_2$ (*I*, indicated as the α-isomer), of which the structure is reported here.

For the platinum thiocyanate complexes several products were obtained, whose composition varies because of easy oxidation. The structure of the complex, analyzing as $Pt(dmtp)_2(NCS)_3$ (*II*), has been determined and is also reported in the present paper.

Experimental

Preparation

α-$Cu(dmtp)_2(NCS)_2$ (*I*) was prepared from copper(II) thiocyanate, freshly precipitated from copper(II) nitrate and ammonium thiocyanate in water. Copper(II) thiocyanate (2 mmol, 0.360 g) was stirred with a solution of dmtp (4 mmol, 0.593 g) in methanol (20 ml). When all copper thiocyanate had dissolved the solution was filtrated and concentrated by slow evaporation. Green needles of α-$Cu(dmtp)_2(NCS)_2$ were deposited. The product was washed with water, acetone and diethyl ether. The yield was about 60%. The compound analyzed as follows; found (calculated): C, 40.05 (40.37); H, 3.46 (3.39); N, 28.99 (29.42); Cu, 13.6 (13.35)%.

$Pt(dmtp)_2(NCS)_3$ (*II*) was prepared by reacting dmtp (4 mmol, 0.593 g) with potassium tetrathiocyanatoplatinate(II) (1 mmol, 0.506 g) in water. An orange-brown precipitate resulted which was recovered and, after drying, was recrystallized from a nitromethan-tetrahydrofuran mixture. Red-orange crystals separated upon standing for several days. After filtration the crystals were washed with tetrahydrofuran and dried in air. The yield was about 18%. *Anal.*, Found (calculated): C, 31.10 (30.67); H, 2.58 (2.42); N, 22.92 (23.15)%. The ligand dmtp has been prepared according to the method of Bülow and Haas [4] from 2,5-pentanedione and 3-amino-1,2,4-triazole. Elemental analyses were performed by the Microanalytical Laboratory of Pascher, Bonn, W. Germany.

Spectroscopic Data

Infrared spectra were taken on a Perkin Elmer Model 580B IR Spectrophotometer as nujol mulls between KRS-5 and polythene (below 400 cm^{-1}) windows and as CsCl discs (concentration about 1%). Ligand field spectra were recorded at room temperature on a Beckman DK2-A UV-vis-NIR spectrophotometer in the solid state, by means of the diffuse reflectance technique using MgO as a reference.

X-Ray Data Collection of the Complexes I *and* II

A green-black elongated prismatic crystal of *I* (of dimensions *ca.* 0.10 × 0.12 × 0.32 mm) and a red-orange roughly prismatic crystal of II (of dimensions *ca.* 0.06 × 0.19 × 0.21 mm) were used for the X-ray analyses. Preliminary cell parameters for both compounds, obtained by rotation and Weissenberg photographs, were subsequently refined by a least-square procedure applied to the θ values of 29(*I*) and 27(*II*) reflections, carefully measured on a Siemens AED single-crystal diffractometer.

The crystal data are as follows:

Complex *I*: $C_{16}H_{16}CuN_{10}S_2$, M = 476.0, Monoclinic, a = 19.088(7), b = 11.516(8), c = 20.118(7) Å, β = 104.51(4)°, U = 4281(4) Å^3, Z = 8, D_c = 1.48 g cm^{-3}, $F(000)$ = 1944, Cu-Kα radiation, $\bar{\lambda}$ = 1.54178 Å; μ(Cu-Kα) = 34.21 cm^{-1}. Space group $C2/c$ from systematic absences and structure determination.

Complex *II*: $C_{34}H_{32}N_{22}Pt_2S_6$, M = 1331.3, Monoclinic, a = 16.914(8), b = 11.474(9), c = 11.893(7) Å, β = 91.52(4)°, U = 2307(3) Å^3, Z = 2, D_c = 1.92 g cm^{-3}, $F(000)$ = 1284, Mo-Kα radiation, $\bar{\lambda}$ = 0.71069 Å; μ(Mo-Kα) = 64.34 cm^{-1}. Space group $P2_1/n$ from systematic absences.

Intensities were collected at room temperature using the Ni-filtered Cu-Kα radiation for *I* and Nb-filtered Mo-Kα radiation for *II* with the ω–2θ scan technique. All the reflections in the range of $6 < 2\theta < 130°$ for *I* and $6 < 2\theta < 48°$ for *II* were measured. Of 3648(*I*) and 3637(*II*) independent reflections, 1535(*I*) and 1136(*II*) having $I > 2\sigma(I)$ were considered as observed and used in the analyses.

The intensities were corrected for the usual Lorentz and polarization factors, but no absorption correction was applied. Both structures were solved by Patterson and Fourier methods and the refinements were carried out by least-squares full-matrix cycles, using the SHELX system of computer programs [5] with first isotropic and then anisotropic thermal parameters for all the non-hydrogen atoms (*I*) and for the platinum atoms only (*II*). All the hydrogen atoms of *I* were localized directly from a difference synthesis and refined isotropically; the hydrogen atoms of *II* were placed in the geometrically calculated positions and included in the final structure factor calculations with isotropic thermal parameter. The final conventional R values were 0.044 for *I* and 0.051 for *II* (observed reflections only). Unit weights were used in each stage of the refinement of both compounds, by analyzing the variations of $|\Delta F|$ as a function of $|F_o|$.

TABLE I. Fractional Atomic Coordinates of the Non-Hydrogen Atoms ($\times10^4$) for *I* with e.s.d.s in Parentheses.

	x/a	*y/b*	*z/c*
Cu	1340(1)	3973(1)	110(1)
S1	−566(1)	6254(2)	−1165(2)
S2	364(2)	1004(3)	−1399(1)
N1	574(4)	4835(7)	−524(4)
N2	1001(5)	2558(7)	−407(5)
N31	2659(4)	4381(6)	1709(4)
N51	2974(4)	2399(6)	1630(4)
N71	2780(4)	1503(7)	1184(4)
N91	2128(4)	3084(6)	771(4)
N32	2922(4)	5511(6)	130(4)
N52	2568(4)	6865(6)	880(4)
N72	1969(5)	7080(7)	1118(5)
N92	1791(4)	5497(6)	454(4)
C1	99(5)	5423(8)	−791(5)
C2	725(5)	1915(9)	−825(5)
C11	3567(5)	3415(9)	2585(5)
C21	3147(5)	4394(8)	2308(5)
C41	2578(5)	3374(8)	1375(5)
C61	3492(5)	2400(9)	2228(5)
C81	2274(5)	1956(8)	691(6)
C101	3921(8)	1336(11)	2434(9)
C111	3260(9)	5545(12)	2681(8)
C12	3682(5)	7079(7)	680(5)
C22	3537(4)	6108(8)	237(5)
C42	2455(4)	5899(8)	473(4)
C62	3204(5)	7477(7)	1006(5)
C82	1538(6)	6235(8)	861(5)
C102	3282(8)	8505(10)	1465(8)
C112	4070(7)	5733(10)	−167(7)

TABLE II. Fractional Coordinates ($\times10^3$) and Isotropic Thermal Parameters ($\times10^3$) of the Hydrogen Atoms for *I* with e.s.d.s. in Parentheses.

	x/a	*y/b*	*z/c*	*U*
H11	393(4)	348(7)	312(4)	74(27)
H71	299(4)	63(7)	123(4)	135(27)
H81	204(4)	151(7)	27(4)	92(25)
H101	433(5)	144(9)	290(5)	110(38)
H102	421(5)	108(9)	205(5)	125(36)
H103	358(5)	64(9)	248(5)	98(38)
H111	362(5)	545(8)	317(5)	121(36)
H112	278(5)	586(9)	278(5)	108(41)
H113	347(5)	618(9)	239(5)	126(38)
H12	417(4)	748(7)	77(4)	51(25)
H72	189(5)	775(8)	147(5)	128(35)
H82	99(4)	619(7)	89(4)	60(25)
H104	382(5)	890(8)	154(5)	96(31)
H105	325(5)	825(8)	196(5)	74(35)
H106	288(5)	912(9)	126(5)	84(36)
H114	453(5)	623(8)	−3(4)	96(31)
H115	385(5)	580(8)	−71(5)	157(33)
H116	422(5)	485(9)	−5(4)	109(31)

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

	x/a	*y/b*	*z/c*
Pt1	5000	5000	5000
Pt2	0	5000	5000
S1	−125(10)	6906(15)	4388(14)
S2	1196(9)	4667(12)	4086(13)
S3	598(9)	5591(14)	6737(12)
N1	384(30)	6801(47)	2185(43)
N2	2336(43)	5993(53)	5184(60)
N3	754(51)	8042(38)	6860(74)
N31	3983(23)	4538(33)	2495(33)
N51	3185(20)	3267(31)	3381(29)
N71	3125(25)	2743(40)	4425(37)
N91	4119(20)	4005(31)	4458(27)
N32	5830(21)	2304(28)	4936(28)
N52	6426(19)	2853(26)	3207(24)
N72	6447(21)	3736(28)	2465(27)
N92	5669(17)	4050(24)	3963(22)
C1	165(36)	6776(56)	3032(52)
C2	1877(31)	5489(47)	4750(42)
C3	750(42)	7021(29)	6768(60)
C11	3014(30)	3527(47)	1481(45)
C21	3603(36)	4204(50)	1481(50)
C41	3781(24)	3980(38)	3436(35)
C61	2771(39)	2908(63)	2405(56)
C81	3709(27)	3287(42)	5014(38)
C101	2201(36)	1936(64)	2502(51)
C111	3849(34)	4994(74)	527(45)
C12	6700(30)	1082(45)	3915(36)
C22	6184(24)	1306(33)	4788(32)
C42	6010(22)	3058(27)	4143(27)
C62	6804(27)	1798(32)	3073(38)
C82	5970(24)	4407(36)	2969(30)
C102	7289(32)	1618(50)	2072(47)
C112	6039(33)	508(46)	5731(40)

TABLE IV. Calculated Fractional Coordinates ($\times10^4$) of the Hydrogen Atoms for *II*.

	x/a	*y/b*	*z/c*
H11	2677	3425	703
H81	3821	3124	5898
H101	1930	1759	1687
H102	1750	2173	3086
H103	2508	1167	2804
H111	3552	4725	−245
H112	4481	4936	432
H113	3689	5883	716
H12	7030	276	3935
H82	5808	5243	2614
H104	7541	753	2097
H105	7758	2256	2067
H106	6922	1713	1321
H114	6337	−309	5590
H115	5411	356	5790
H116	6262	893	6505

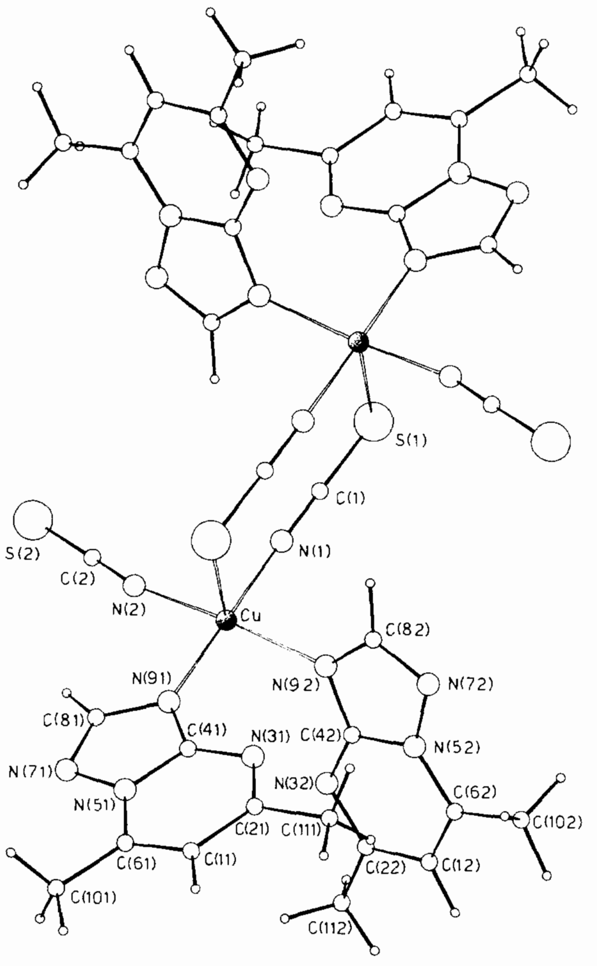

Fig. 1. Perspective view of the dimeric unit [Cu(dmtp)$_2$(NCS)$_2$]$_2$ in *I* with the atomic numbering scheme.

Final atomic coordinates are given in Tables I–II for *I* and III–IV for *II*. Atomic thermal parameters and a list of calculated and observed structure factors for both compounds are available from the authors on request.

All the calculations were performed on the CYBER-76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna, with the financial support from the University of Parma.

Discussion

Spectroscopic Properties

The IR spectra of both complexes *I* and *II* show all the bands present in the spectrum of the free ligand. In addition bands are observed due to the thiocyanate ions. As usually observed in coordination compounds, there are several differences in intensity and minor shifts for the ligand absorptions in the fingerprint area.

The anion absorptions of the copper compound indicate two different thiocyanate groups. This is shown by two ν_{CN} absorptions at 2120 and 2079 cm^{-1}. The former is indicative of N,S-bridging and the latter of N-terminal coordination [6]. Likewise two bands are also found for the ν_{CS} vibrations. ν_{CS} of the N-terminal bound NCS is assigned to the 831 cm^{-1} absorption, while ν_{CS} of the bridging anion is assigned to the 782 cm^{-1} absorption. Two δ_{NCS} absorptions are observed: 473 and 463 cm^{-1}. Since δ_{NCS} absorptions of bridging thiocyanate are usually split, overlapping of absorptions may be present. Therefore, no detailed assignment of these bending vibrations can be made.

TABLE V. Relevant Bond Distances (Å) and Angles (°) with e.s.d.s. in *I*.

i) in the coordination polyhedron			
Cu–N(1)	1.953(8)	Cu–N(92)	2.000(7)
Cu–N(2)	1.954(9)	Cu–S(1^i)	2.886(4)
Cu–N(91)	2.019(8)		
N(1)–Cu–N(2)	89.0(4)	N(1)–Cu–S(1^i)	95.1(2)
N(1)–Cu–N(92)	88.1(3)	N(2)–Cu–S(1^i)	98.8(3)
N(2)–Cu–N(91)	91.2(3)	N(91)–Cu–S(1^i)	84.5(2)
N(91)–Cu–N(92)	91.8(3)	N(92)–Cu–S(1^i)	94.6(2)
ii) in the isothiocyanate groups			
N(1)–C(1)	1.151(12)	N(2)–C(2)	1.145(13)
C(1)–S(1)	1.617(10)	C(2)–S(2)	1.584(10)
N(1)–C(1)–S(1)	179.8(9)	N(2)–C(2)–S(2)	178.4(9)
C(1)–N(1)–Cu	167.7(8)	C(2)–N(2)–Cu	163.8(9)
C(1)–S(1)–Cu^i	95.2(4)		

(continued on facing page)

TABLE V. *(continued)*

iii) in the organic ligands

C(11)–C(21)	1.414(13)	C(12)–C(22)	1.413(13)
C(11)–C(61)	1.361(14)	C(12)–C(62)	1.331(14)
C(21)–N(31)	1.326(12)	C(22)–N(32)	1.331(11)
C(21)–C(111)	1.512(17)	C(22)–C(112)	1.515(16)
N(31)–C(41)	1.330(12)	N(32)–C(42)	1.334(11)
C(41)–N(51)	1.379(12)	C(42)–N(52)	1.366(11)
C(41)–N(91)	1.343(12)	C(42)–N(92)	1.341(11)
N(51)–N(71)	1.357(11)	N(52)–N(72)	1.368(13)
N(51)–C(61)	1.352(12)	N(52)–C(62)	1.371(12)
C(61)–C(101)	1.474(17)	C(62)–C(102)	1.486(16)
N(71)–C(81)	1.307(13)	N(72)–C(82)	1.295(13)
C(81)–N(91)	1.343(12)	C(82)–N(92)	1.351(13)
C(21)–C(11)–C(61)	120.2(9)	C(22)–C(12)–C(62)	122.2(9)
C(11)–C(21)–N(31)	123.3(8)	C(12)–C(22)–N(32)	122.4(8)
C(11)–C(21)–C(111)	120.5(9)	C(12)–C(22)–C(112)	120.8(8)
N(31)–C(21)–C(111)	116.2(9)	N(32)–C(22)–C(112)	116.7(9)
C(21)–N(31)–C(41)	115.8(8)	C(22)–N(32)–C(42)	114.8(8)
N(31)–C(41)–N(51)	122.6(9)	N(32)–C(42)–N(52)	123.9(8)
N(51)–C(41)–N(91)	107.5(8)	N(52)–C(42)–N(92)	107.7(7)
C(41)–N(51)–C(61)	122.7(8)	C(42)–N(52)–C(62)	121.9(8)
N(71)–N(51)–C(41)	109.9(8)	N(72)–N(52)–C(42)	109.7(7)
C(11)–C(61)–N(51)	115.3(9)	C(12)–C(62)–N(52)	114.6(8)
C(11)–C(61)–C(101)	126.0(9)	C(12)–C(62)–C(102)	127.3(9)
N(51)–C(61)–C(101)	118.7(9)	N(52)–C(62)–C(102)	118.1(9)
N(51)–N(71)–C(81)	103.0(8)	N(52)–N(72)–C(82)	103.1(8)
N(71)–C(81)–N(91)	115.5(9)	N(72)–C(82)–N(92)	115.3(9)
C(41)–N(91)–C(81)	104.1(8)	C(42)–N(92)–C(82)	104.2(8)

Asymmetric unit: i –*x*, 1 – *y*, –*z*

The platinum compound (*II*) shows only one sharp ν_{CN} absorption at 2123 cm^{-1}, a weak ν_{CS} at 696 cm^{-1} and several weak δ_{NCS} absorptions around 455 cm^{-1}. These values indicate a S-coordination and agree with those found in other $Pt(SCN)_6^{2-}$ complexes [7].

The ligand field spectrum of *I* shows one broad maximum around 14.7·10^3 cm^{-1} without any significant shoulders. Band maxima in this range agree with tetragonally-based five and six coordinate Cu(II) species [8].

Description of the Crystal Structures

The crystal structure of *I* (Fig. 1) consists of centrosymmetric dimeric units $[Cu(dmpt)_2(NCS)_2]_2$, in which two thiocyanate groups bridge the copper atoms forming an eight-membered ring. The coordination polyhedron around each copper atom is an elongated square pyramid which involves two nitrogen atoms from the isothiocyanate ligands and two triazole nitrogen atoms from two dmtp ligands in the basal coordination plane and a thiocyanate sulphur atom from the centrosymmetric complex in the apical position. The Cu–N$_{(NCS)}$ bond lengths (1.953(8), 1.954(9) Å) are significantly shorter than the Cu–N$_{(dmtp)}$ bond distances (2.019(8), 2.000(7) Å), in good agreement with literature values [9, 10]. The four atoms of the basal plane show a tetrahedral distortion with the Cu atom displaced from their mean plane of 0.096(2) Å, towards the sulphur apical atom. The Cu–S apical bond length of 2.886(4) Å, much longer than a normal Cu–S single bond (2.39 Å), is comparable with the value of 2.846 Å found in the structure of thiocyanato(2-dipropylaminoethanolato)copper(II) [10] where a thiocyanate sulphur atom from an oxygen-bridged dinuclear unit approaches the Cu atom of the adjacent unit forming a distorted tetragonal pyramid. The Cu···Cu distance of 5.552 Å in the dimeric unit of *I* agrees with those found in the structures of μ-dithiocyanato-tetrakis(methyldiphenylphosphine)dicopper(II) (5.30 Å) [11], di-μ-thiocyanato-bis[di(3-aminopropyl)amine]dicopper(II) perchlorate (5.53 Å) [12] and thiocyanato(2-dipropylaminoethanolato)copper(II) (5.727 Å) [10], where the thiocyanate ligands bridge the metal atoms *via* the

TABLE VI. Relevant Bond Distances (Å) and Angles (°) with e.s.d.s in *II*.

i) in the coordination polyhedra			
		Pt(2)–S(1)	2.31(2)
Pt(1)–N(91)	1.97(3)	Pt(2)–S(2)	2.35(2)
Pt(1)–N(92)	2.02(3)	Pt(2)–S(3)	2.37(1)
N(91)–Pt(1)–N(92)	85.3(9)	S(1)–Pt(2)–S(2)	94.6(5)
		S(1)–Pt(2)–S(3)	92.1(6)
		S(2)–Pt(2)–S(3)	95.5(5)
ii) in the thiocyanate groups			
N(1)–C(1)	1.08(8)	C(2)–S(2)	1.67(5)
C(1)–S(1)	1.70(6)	N(3)–C(3)	1.18(6)
N(2)–C(2)	1.09(9)	C(3)–S(3)	1.66(4)
N(1)–C(1)–S(1)	173(6)	C(2)–S(2)–Pt(2)	106(2)
C(1)–S(1)–Pt(2)	101(2)	N(3)–C(3)–S(3)	170(7)
N(2)–C(2)–S(2)	178(6)	C(3)–S(3)–Pt(2)	111(3)
iii) in the organic ligands			
C(11)–C(21)	1.26(8)	C(12)–C(22)	1.40(6)
C(11)–C(61)	1.38(9)	C(12)–C(62)	1.31(6)
C(21)–N(31)	1.40(7)	C(22)–N(32)	1.31(5)
C(21)–C(111)	1.52(9)	C(22)–C(112)	1.47(6)
N(31)–C(41)	1.34(6)	N(32)–C(42)	1.32(5)
C(41)–N(51)	1.30(5)	C(42)–N(52)	1.35(4)
C(41)–N(91)	1.33(5)	C(42)–N(92)	1.29(4)
N(51)–N(71)	1.39(6)	N(52)–N(72)	1.34(4)
N(51)–C(61)	1.40(8)	N(52)–C(62)	1.38(5)
C(61)–C(101)	1.48(9)	C(62)–C(102)	1.48(7)
N(71)–C(81)	1.35(6)	N(72)–C(82)	1.28(5)
C(81)–N(91)	1.27(6)	C(82)–N(92)	1.36(5)
C(21)–C(11)–C(61)	125(5)	C(22)–C(12)–C(62)	123(5)
C(11)–C(21)–N(31)	121(5)	C(12)–C(22)–N(32)	124(4)
C(11)–C(21)–C(111)	127(6)	C(12)–C(22)–C(112)	125(4)
N(31)–C(21)–C(111)	111(5)	N(32)–C(22)–C(112)	111(4)
C(21)–N(31)–C(41)	118(4)	C(22)–N(32)–C(42)	111(3)
N(31)–C(41)–N(51)	118(4)	N(32)–C(42)–N(52)	127(3)
N(51)–C(41)–N(91)	112(4)	N(52)–C(42)–N(92)	105(3)
C(41)–N(51)–C(61)	127(4)	C(42)–N(52)–C(62)	120(3)
N(71)–N(51)–C(41)	108(4)	N(72)–N(52)–C(42)	116(3)
C(11)–C(61)–N(51)	111(5)	C(12)–C(62)–N(52)	113(4)
C(11)–C(61)–C(101)	131(6)	C(12)–C(62)–C(102)	128(4)
N(51)–C(61)–C(101)	118(5)	N(52)–C(62)–C(102)	119(4)
N(51)–N(71)–C(81)	101(4)	N(52)–N(72)–C(82)	97(3)
N(71)–C(81)–N(91)	116(4)	N(72)–C(82)–N(92)	119(4)
C(41)–N(91)–C(81)	104(4)	C(42)–N(92)–C(82)	103(3)

nitrogen and the sulphur atoms to form eight-membered rings. Also in *I*, the eight-membered ring is only approximately planar, the displacement of the copper atom being 0.208 Å above and below the plane passing through the two bridging thiocyanate groups. The dihedral angle between the plane Cu_2S_2-C_2N_2 and the basal coordinating plane of the pyramid is 92°. The dimensions of the NCS groups and the angles Cu–N–C suggest a partial sp^2 hybridization of nitrogen and sulphur atoms for the N-bonded thiocyanate ligands. The crystal structure of *II* (Figs. 2 and 3) which is a mixed-valence compound, contains both octahedral $[Pt(SCN)_6]^{2-}$ anions and square planar $[Pt(dmtp)_4]^{2+}$ cations; the Pt(IV)–S distances of 2.31, 2.35 and 2.37 Å are comparable with those found in the structure

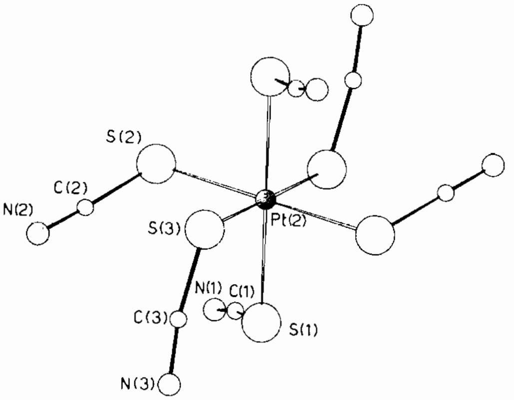

Fig. 2. Perspective view of the $[Pt(SCN)_6]^{2-}$ anion in *II*.

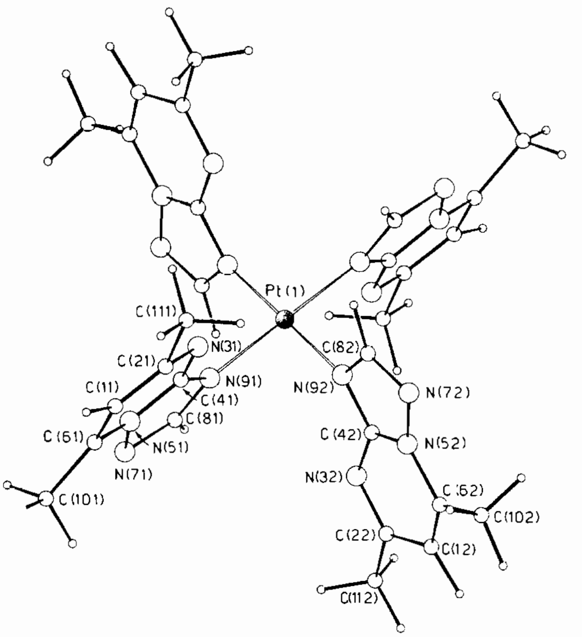

Fig. 3. Perspective view of the $[Pt(dmtp)_4]^{2+}$ cation in *II* with the atomic numbering scheme.

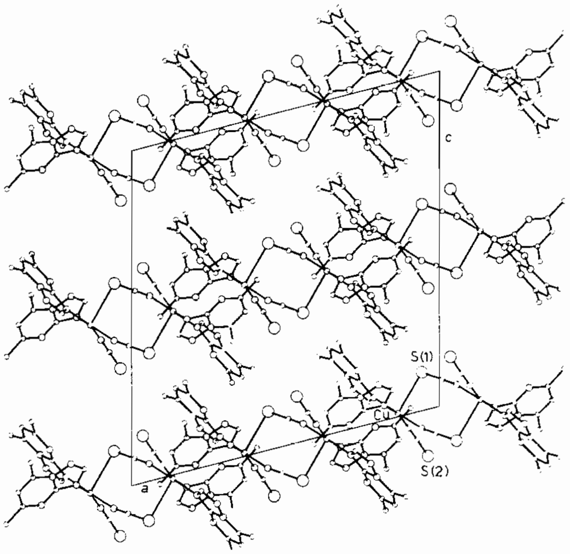

Fig. 4. Projection along *b* of the structure of *I*.

of pentakis(dimethylsulfoxide)oxovanadium hexakis(thiocyanato)platinum(IV) (2.355–2.387 Å) [13] which represents the only known example of a structure containing the $[Pt(SCN)_6]^{2-}$ anion that has been characterized by X-ray structure determination.

The N–C and the C–S bond distances and the Pt–S–C angles are consistent with those found for the S-bonded thiocyanate groups in the structures of *cis*-thiocyanatoisothiocyanato-bis(3,3-dimethylbutynyl-diphenylphosphine)platinum(II) [14] and potassium bis(oxalato)bis(thiocyanato)platinum(II) tetrahydrate [15]. The Pt(II)-N distances of 1.97 and 2.02 Å in the square planar cation agree with those found in tetrakis(*N*-methylimidazole)platinum(II) hexachloroplatinate(IV) [16] where heterocyclic nitrogen donor ligands are present.

In both compounds all the dmtp molecules act as a monodentate ligand through the triazole N_3 nitrogen atom, the pyrimidine N_4 nitrogen atom being excluded from participating in any coordination. The behaviour of the dmtp ligand differs from that of adenine and hypoxanthine, which present a distinct tendency to coordinate to the metal ions through both the high electron density N_3 and N_9 centers (see purine scheme) and through N_7 when N_9 is blocked, and resembles that of guanine where the N_9 binding site seems favoured by the metal ions in the coordination.

A comparison between the structural parameters of the 1,2,4-triazolo[1,5-α]pyrimidine moiety in the dmtp ligand in *I* and *II* and those of the corresponding moiety in the uncomplexed 6-ethoxycarbonyl-4-ethyl-1,2,4-triazolo[1,5-α]-pyrimidin-7(4H)-one shows that the binding of the metal atom to the triazole nitrogen atom has a real effect on the ligand geometry only near N_3, having the fused-ring systems different substituents; significant differences are found for the bond angles involving this nitrogen.

The analysis of the planarity data of the dmtp ligands indicates that the fused-ring systems of the two dmtp molecules in both compounds are planar. The mean planes through the nine-framework of the two independent dmtp ligands make angles with the mean basal coordination plane of 16 and 67° in the copper compound and of 64 and 105° in the platinum complex.

In *I* the dimeric units are joined in chains, running along *a* (Fig. 4) by stacking interactions: the inversion-related dimers [about ¼, ¼, 0] show

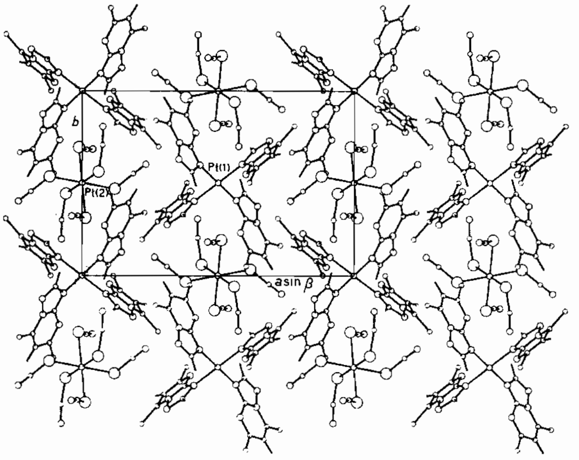

Fig. 5. Projection along *c* of the structure of *II*.

significant overlap involving pyrimidine and triazole moieties of half of the dmtp molecules (the mean separation between the nine-ring frameworks is 3.41 Å). In this situation the uncoordinated triazole nitrogen of the nine-ring framework of the remaining dmtp from a dimer comes within 3.477(8) Å of the copper atom of adjacent dimer and approximately occupies the sixth position around the metal.

In *II* the packing is determined by van der Waals contacts (Fig. 5), and no stacking interactions are observed.

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References

1 J. G. Haasnoot and W. L. Groeneveld, *Z. Naturforsch., 32b,* 533 (1977).
2 P. de Meester and A. C. Skapski, *J. Chem. Soc. (A),* 2167 (1971).
3 J. Dillen, J. G. Haasnoot, A. T. H. Lenstra and J. Reedijk, *Polyhedron,* in press.
4 C. Bülow and K. Haas, *Ber. Dtsch. Chem. Ges., 42,* 4638 (1909).
5 G. M. Sheldrick, *System of Computing Programs,* University of Cambridge (1976).
6 R. J. H. Clark and C. S. Williams, *Spectrochimica Acta, 22,* 1081 (1966).
7 A. Sabatini and I. Bertini, *Inorg. Chem., 4,* 959 (1965).
8 B. J. Hathaway and D. E. Billing, *Coord. Chem. Revs., 5,* 143 (1970).
9 M. Cannas, G. Carta and G. Marongiu, *J. Chem. Soc., Dalton,* 533 (1974).
10 M. Mikuriya, Y. Nishida, S. Kida, T. Uechi and I. Ueda, *Acta Cryst., B33,* 538 (1977).
11 A. P. Gaughan, R. F. Ziolo and Z. Dori, *Inorg. Chim. Acta, 4,* 640 (1970).
12 M. Cannas, G. Carta and G. Marongiu, *Gazzetta Chimica Italiana, 104,* 581 (1974).
13 T. S. Khodashova, M. A. Porai-Koshits, V. S. Sergienko, Yu. A. Buslaev, A. A. Kuznetsova, V. V. Kovalev, L. A. Butman, *Koord. Khim., 4,* 941 (1978).
14 S. Wong, S. Jacobson, P. C. Chieh and A. J. Carty, *Inorg. Chem., 13,* 284 (1974).
15 A. C. Villa, A. G. Manfredotti, A. Giacomelli, C. Guastini and A. Indelli, *Inorg. Chem., 14,* 1654 (1975).
16 M. Biagini Cingi, A. M. Manotti Lanfredi, A. Tiripicchio, C. G. van Kralingen and J. Reedijk, *Inorg. Chim. Acta, 39,* 265 (1980).
17 J. P. Clayton, N. H. Rogers, V. J. Smith, R. Stevenson and T. J. King, *J. Chem. Soc. Perkin I,* 1347 (1980).